

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM

PROCEEDINGS

VOLUME XL

No. 1

President: J. VAN DER HOEVE

Secretary: B. BROUWER

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Chemistry. — *On the Relative and Absolute Spatial Configuration of Isomorphous, Optically-active Complex Salts of Trivalent Cobaltum and Rhodium: I. Comparison of the Triethylenediamine- and Tricyclohexanediamine-Salts.* By F. M. JAEGER.

(Communicated at the meeting of December 19, 1936).

§ 1. In recent years the problem concerning the absolute configuration of optically-active ions in complex metallic salts of the *tridiamino-* and *tri-biacido-*type has, from the side of several investigators, met with an increasing interest. The significance of this question is clear, because it is intimately connected with that concerning the role of the central metallic ions, like Cr^{+++} , Co^{+++} , Rh^{+++} , Ir^{+++} , Pt^{++++} , etc. in such compounds and their influence upon the particular manifestation of the often enormous rotatory power, upon the apparently rather capricious phenomena of the rotatory dispersion and the more or less strong circular dichroism exhibited by these remarkable, relatively simply built chemical substances.

WERNER¹⁾, on comparing the properties of the optically-active *triethylenediamine-cobaltic-* and *rhodium-*salts of the type²⁾: $\{Co(Ene)_3\}X_3$ and $\{Rh(Ene)_3\}X_3$, in 1912 drew the conclusion that the replacement of the central *cobaltum*-atom by a *rhodium*-atom and vice-versa in the antipodes having the same spatial configuration, evidently was accompanied by a *reversion* of the algebraic sign of the original rotation. As to a general criterium, in how far in such cases one has to deal with ions of really the same absolute spatial arrangement, WERNER suggested that *optically-active ions of analogous spatial configurations, if combined with one and the same optically-active substance, always will furnish compounds showing analogous relations of their solubilities.*

Thus, because $\{Co(Ene)_3\}Br_3$, for instance, when being resolved into its antipodes by means of its *bromo-d-tartrates*, yields the *bromo-d-tartrate* of the *dextrogyratory* ion as the *least-soluble* product, whilst $\{Rh(Ene)_3\}Br_3$ under the same circumstances as the *least-soluble bromo-d-tartrate* yields that of the *levogyratory* ion, — it follows that the substitution of the *Co*-atom in complex ions of the same spatial architecture by a *Rh*-atom evidently in this special case causes a *reversion* of the direction of the optical rotation. This view can beforehand be considered in so far as rather vague and undefined, as the "rotation" of many of these compounds can as well be positive as negative as a consequence of their special and

¹⁾ A. WERNER, Ber. d. d. chem. Ges., **45**, 1229 (1912).

²⁾ In this paper the diamines introduced into the complex ions are indicated by the abbreviations: (*Ene*) = *ethylenediamine*; (*Cptn*) = *cyclopentanediamine*; (*Chxn*) = *cyclohexanediamine*; etc.

often highly deviating rotatory dispersion for different wave-lengths; whilst it can hardly be stated which special wavelengths are to be considered as really "corresponding" ones for the purpose of comparison of the complex salts of different series. But besides this, also other objections can be advanced against the said conclusion, to which the present author has already drawn attention¹⁾ in 1917. The *general* applicability of WERNER'S solubility-rule as stated above, can also be doubted because of the fact that the "solubility" is a highly complicated property of matter which depends on many other factors, besides spatial configuration. Therefore, the view was suggested that as a final criterium in such questions the crystallographical relations between the compounds compared might more advantageously be used, because the crystalform is a property highly sensitive to any change of spatial configuration and in this connection thus might be considered as a more reliable phenomenon; and this in the present case the more so, as for the Co^{+++} - and Rh^{+++} -compounds considered, the rigorous *isomorphous* replacement of the two metals there-in was previously demonstrated as well in the case of the racemic, as in that of the optically-active salts of the two series. Since that time this view has, on several occasions, been contested by a number of authors on this subject²⁾ and, — at least in the case of the *triethylenediamine*-salts, — evidently with success. But notwithstanding this, the problem yet appears to be not completely settled in all its aspects, as will become clear from the present paper. Now several series of compounds of this kind have been investigated in this laboratory, so that we can now much better survey the complete experimental material. The time, therefore, has come for making a tentative to rightly co-ordinate the different data obtained, in the hope that, by a detailed and systematic discussion of them, a clearer insight into the prevailing relations may be gained.

§ 2. The experiments to be discussed relate to the introduction of the bases: *ethylenediamine*, racemic and *d*- and *l*-*cyclohexanediamine*³⁾ racemic, *d*- and *l*-*cyclopentanediamine*⁴⁾, racemic, *d*- and *l*- β -2-4-*norm. pentane-diamine*⁵⁾ and α -2-4-(*meso*)-*norm. pentanediamine*⁵⁾ into the

¹⁾ F. M. JAEGER, Chem. Weekbl., **14**, 718 (1917); Rec. d. Trav. d. Chim. d. Pays-Bas, **38**, 171 (1919); Rev. génér. des Sciences, **30**, 298 (1919); Confér. dev. la Soc. chim. de France, Bull. d. la Soc. chim. (4), **27**, (1920), 173; *Lectures on the Principle of Symmetry*, 2nd Ed., 251 (1920); *Le Principe de Symétrie*, Paris, 294 (1924); *Spatial Arrangements of Atomic Systems and Optical Activity*, New York, 92 (1930); cf. also: J. MEISENHEIMER, etc., Ann. d. Chem., **449**, 190 (1926).

²⁾ M. DÉLÉPINE, Bull. Soc. chim. de France, (4), **55**, 1256, 1226 (1934); M. DÉLÉPINE and R. CHARONNAT, Bull. Soc. minéral. franç., **53**, 73 (1930); W. KUHN and K. BEIN, Zeits. f. anorg. Chem., **216**, 323, 335, 336 (1934) etc.

³⁾ In a finished but not yet published paper with L. BIJCKER.

⁴⁾ F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chem., **175**, 197, 203, 214, 215, 228 (1928); etc.

⁵⁾ C. J. DIPPEL and F. M. JAEGER, Rec. d. Trav. d. Chim. d. Pays-Bas, **50**, 547 (1931).

complex ions. In this paper, chiefly salts will be compared which are derived from *ethylenediamine* and *cyclohexanediamine* and which in all cases correspond to the *least-soluble chloro- or bromo-d-tartrates* used in the fission-experiments, so as to facilitate the general survey of the facts and to prevent confusion. The corresponding *cyclopentanediamine*-salts will be treated in the following paper. The prefixes *d-* and *l-* will be used to denote the *dextro-* and *levogyrotory* antipodes of the optically-active *diamines* used; the prefixes *D-* and *L-* to denote the rotation of the resolved (complex) ions *in the red part* of the visible spectrum, without regarding the occasional change of the sign of the rotation for other wave-lengths.

Then it must be borne in mind that in all cases where three identical molecules of an optically-active *diamine* were introduced into the complex ions, we always stated the fact first observed by SMIRNOFF¹⁾ (with optically-active *α-propylenediamine*), that in these reactions a typical *dissymmetrical* synthesis takes place, so that of all theoretically imaginable isomerides exclusively only *two* are produced: thus, of all isomerides imaginable when *d-* or *l-cyclopentane-* or *cyclohexanediamines* are used, *only* the combinations: $D-\{Co(l-Cptn)_3\}'''$, $L-\{Co(d-Cptn)_3\}'''$, $D-\{Rh(l-Chxn)_3\}''$, $L-\{Rh(d-Chxn)_3\}'''$, etc. prove to be generated in these reactions, with a yield of 100 %, — as well in the *Co-*, as in the *Rh-series*. All other combinations: $D-\{(d_3)\}'''$, $L-\{(l_3)\}'''$, also: $\{d_2l\}'''$ or $\{dl_2\}'''$, — be it in *D-* or *L-*ions, — seem to be excluded in this kind of syntheses. In several cases the *instability* of the latter combinations could directly be demonstrated by their subsequent rapid decomposition in solution, for instance, according to the equation: $3\{d_2l\}''' \rightarrow [\{d_3\}''' + \{l_3\}'''] + \{d_3\}'''$; etc. Moreover, in all cases it could be proved by means of crystallographical evidence, that the *racemic* compounds of the series investigated *exclusively* exist of combinations of equal numbers of molecules of the types: $D-\{(l_3)\}'''$ and $L-\{(d_3)\}'''$; this demonstration could be made, because the crystallographical character of all the racemates here investigated is *quite different* from that of the composing optically-active compounds and their formation thus could rigorously be verified in all prevailing cases. When desired, these facts were still controlled afterwards by means of X-ray powder-spectrograms.

§ 3. A second fact which must be kept in mind is that, which was first emphasised by TSCHUGAEFF and SOKOLOW²⁾ in the case of *α-propylenediamine*-derivatives; namely, that the contribution of the optically-active *diamines* to the rotation of the complex salts into which they are introduced, appears not only *much greater* than that of the free bases, but always to *have the opposite algebraic sign*. Thus, for instance,

¹⁾ A. P. SMIRNOFF, *Helv. Acta Chim.*, **3**, 178 (1920).

²⁾ L. TSCHUGAEFF and W. SOKOLOW, *Ber. d. d. chem. Ges.*, **40**, 3464 (1907); **42**, 57 (1909).

$\{Rh(d\text{-}Base)_3\}X_3$ is strongly levogyrotory, $\{Rh(l\text{-}Base)_3\}X_3$ is dextrogyrotory, etc.

On the other hand, the relatively high situation of the curve IV in Fig. 4 with respect to the curve I for *L*-triethylenediamine-rhodium-chloride, makes it highly probable that also in the levogyrotory tri- β -2-4-norm. pentanediamine-rhodium-salt, — which has the constitution: *L*- $\{Rh(l\text{-}Base)_3\}Cl_3$, — the contribution to the rotation of the complex salt is in reality positive, i.e. also opposite to that of the free base involved.

§ 4. As to the least-soluble chloro- or bromo-*d*-tartrates used in the fission of the racemic compounds here considered and to the chlorides or bromides isolated from them, the following experiences were gathered.

1. In the case of the triethylenediamine-compounds of Co and Rh the least-soluble chloro- and bromo-*d*-tartrates correspond to *D*- $\{Co(En)_3\}X_3$ and to *L*- $\{Rh(En)_3\}X_3$.

2. In the case of the tricyclohexanediamine-compounds of the two series the least-soluble chloro- and bromo-*d*-tartrates proved to correspond to *L*- $\{Co(d\text{-}Chxn)_3\}X_3$ and to *L*- $\{Rh(d\text{-}Chxn)_3\}X_3$. In this case their constitution was rigorously proved by their direct synthesis from the optically-active diamines and their subsequent destruction, — after which the rotation of the isolated base was determined.

§ 5. By means of DÉLÉPINE's elegant method of "optically-active racemates" it was stated:

1A. From a mixed solution of an equal number of molecules of *L*- $\{Co(En)_3\}Br_3$ and *L*- $\{Rh(En)_3\}Br_3$ crystal aggregates were obtained consisting of very small, rhombohedral crystals which, on X-ray-examination, yielded spectrograms which were identical with those of the ditrigonal racemic compounds. Later-on, some single crystals were deposited from the mother-liquor, which showed the form of the racemic compound:

$c = \{0001\}$; $m = \{10\bar{1}0\}$ and $r = \{10\bar{1}1\}$, with $c:r = 37^\circ 52'$ and $a:c = 1:0,673$. From an analogous mixture of *D*- $\{Co(En)_3\}Br_3$ and *L*- $\{Rh(En)_3\}Br_3$ also multiple aggregations, but this time consisting of mixed crystals, were obtained which, on X-ray-examination, yielded the spectrograms of the tetragonal antipodes¹⁾. From this the conclusion must be drawn that the *L*-salts of Co and Rh in this case have enantiomorphous, the *L*- and *D*-salts of both series, however, the same spatial configurations. These results thus completely confirm those of DÉLÉPINE.

2A. From a mixed solution of equimolar quantities of *L*- $\{Co(d\text{-}Chxn)_3\}Br_3$ and of *L*- $\{Rh(d\text{-}Chxn)_3\}Br_3$ very beautiful, transparent, orange-coloured mixed crystals were deposited of hexagonal-pyramidal

¹⁾ At this moment Mr. J. TER BERG is occupied in this laboratory with an X-ray-examination of a number of racemic and optically-active triethylenediamine-cobaltic- and rhodium-salts; so that now we have already a series of X-ray-spectrograms at our disposal which enable us rapidly to compare such salts in cases like this.

symmetry (Fig. 1A); on the contrary, from a mixed solution of $D\text{-}\{\text{Co}(\text{L-Chxn})_3\}\text{Br}_3$ and $L\text{-}\{\text{Rh}(\text{d-Chxn})_3\}\text{Br}_3$ pale yellow needles with the typical ditetragonal-bipyramidal symmetry of the racemic compound (Fig. 1B)

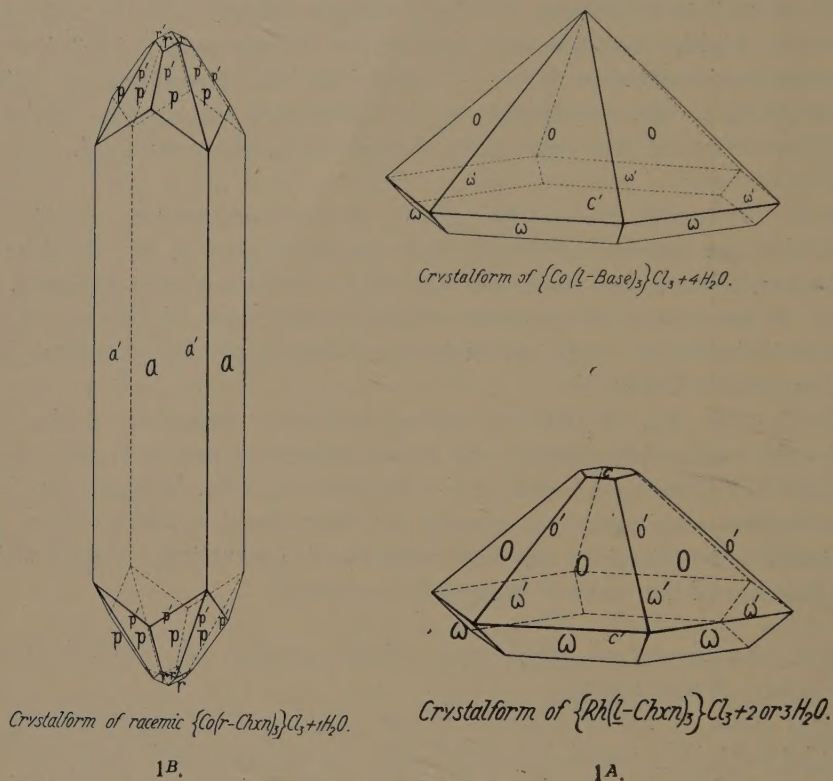


Fig. 1. Crystal forms of the optically-active and of the racemic Tricyclohexanediamine-salts of Cobaltum and Rhodium.

were obtained. These facts prove beyond any doubt, that the L -salts of the two series have the same, the D - and L -salts, however, enantiomorphous spatial configurations.

Whilst, therefore, in the case 1) of the triethylenediamine-salts the compounds of Co and of Rh with the same spatial arrangements exhibit opposite optical rotations, in the case 2) they apparently have rotations of the same algebraic sign in the red part of the spectrum. If, therefore, WERNER's solubility-rule holds, even then the rotations observed apparently are in the two cases not in agreement with each other.

§ 6. For the purpose of a comparison of the rotatory dispersions of these salts and especially for that of the different dispersion-curves obtained with those of the D - and L -triethylenediamine-salts of cobaltum and rhodium, — which, as relating to an optically-inactive base, will be used as standards of reference, — the data for the rotatory dispersion of these salts were once more exactly determined by new measurements and are graphically represented in Fig. 2 and in Fig. 4 respectively.

Moreover, the corresponding data relating to the salts: *monoethylenediamine - di - d - cyclohexanediamine - cobaltic - chloride*; to *diethylene-*

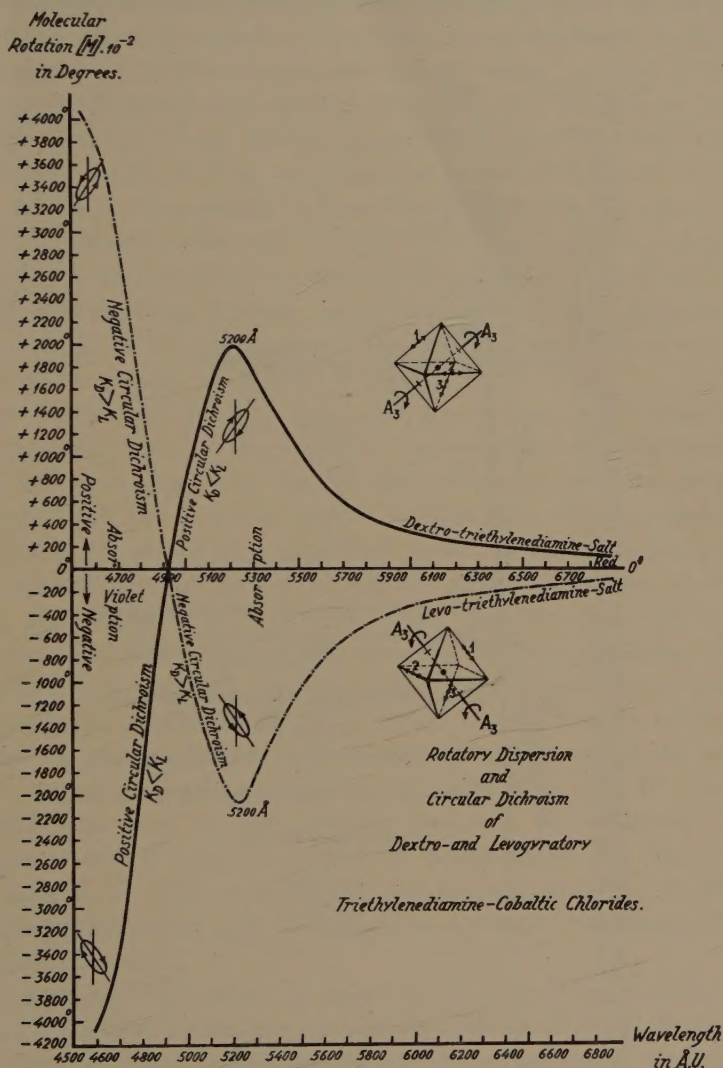


Fig. 2. Rotatory Dispersion of D- and L-Triethylenediamine-Cobaltic-Chloride.

diamine-mono-d-cyclohexanediamine-cobaltic-chloride and to *tri-d-cyclohexanediamine-cobaltic-chloride*, are represented in the graph of Fig. 3.

All these salts correspond to the least soluble *chloro- or bromo-tartrates* and their special constitution was proved by direct, dissymetrical synthesis, starting from the optically-active bases. They represent *triethylenediamine-salts* in which one, two and all three molecules of the base are consecutively substituted by 1, 2 or 3 molecules of the *dextrogyrotory cyclohexanediamine*.

Their dispersion-curves I—III represented in the corresponding graph of Fig. 3, in which simultaneously the dispersion-curve of *dextrogyrotory*

$\{\text{Co}(\text{Ene})_3\}\text{Cl}_3$ is inserted, will be discussed in detail in connection with the different dispersion of the rhodium-salts to be found in Fig. 4. All the numerical data required for the construction of these graphs will later-on be published elsewhere.

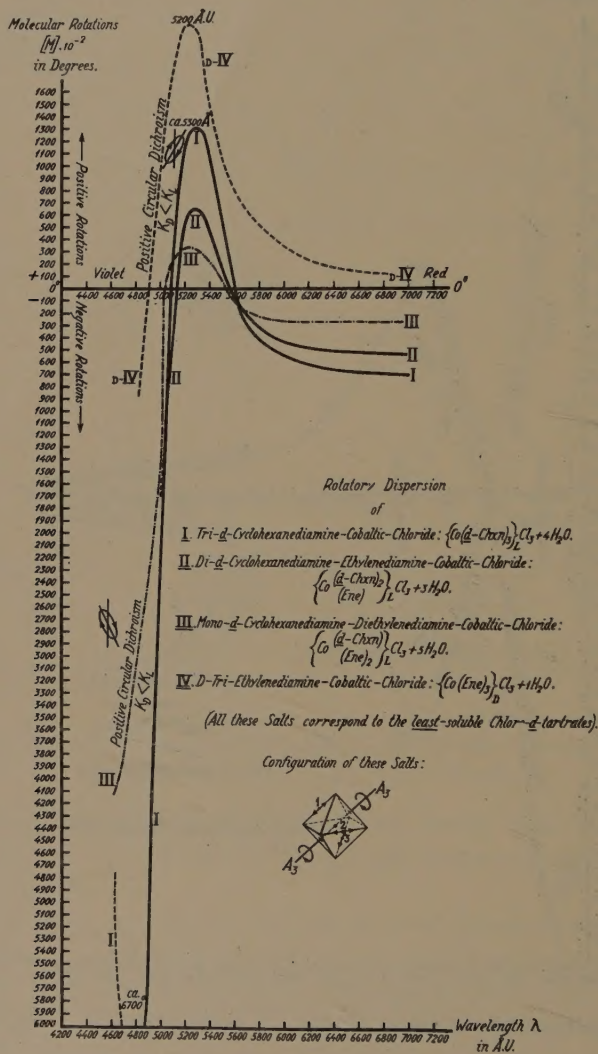


Fig. 3. Rotatory Dispersion of Cyclohexanediamine- and Ethylenediamine-Cobaltic-Salts¹⁾.

§ 7. For the right comparison of these curves, we will start with those represented in Fig. 3.

Evidently the curves I, II, and III prove, that the 1, 2, or 3 molecules of the dextrogyratory base present in these complexes, influence their optical rotation in a way which is almost identical with a simple optical

¹⁾ See about the notation L- in this figure, the Note ¹⁾ at the bottom of the next page.

superposition of their action. If, now, it be kept in mind that this action is *levogyrotory*, — it immediately becomes clear that the rotation due to the complex ion itself may approximately be estimated by a proportional shift upwards of these dispersion-curves. Then, however, there can be no doubt any longer *that all these curves are closely related to that of the dextrogyrotory triethylenediamine-cobaltic-chloride* with its *positive* circular dichroism. Because of the *levogyrotory* influence of the molecules of the *d*-base introduced, the first maximum (at about 5300 A.U.) in the curves I, II, and III has apparently become *lower*, whilst for the same reason the minimum (between 4600 and 4700 A.U.) has got *deeper*: this partially is the cause of the strong *asymmetry* of the three curves with respect to the line of zero-rotation. Exactly as in the case of the *triethylenediamine-salt*, — all the other ones have, — notwithstanding this asymmetry, — yet preserved the *positive* character of their COTTON-effect.

Now KUHN and BEIN¹⁾ some years ago first drew attention to the possible significance of the algebraic sign of the circular dichroism in the absorption-band nearest to the red end of the spectrum for answering the question about the *absolute* spatial configuration of such optically-active compounds. By means of a simplified model in which peripheral oscillations *coupled* with those at the central atom, are taking place in three planes perpendicular to each other, they thought to be able to make it probable, that such complex ions like that of *dextrogyrotory triethylenediamine-cobaltic-chloride* would have the spatial arrangement indicated by the octahedron-scheme in Fig. 2, if certain suppositions be made about the polarisation of the vibrating, electrically charged parts of the ion and the possibility of at least establishing the algebraic sign of the electrical momenta occurring in the adjacent parts of the molecule. *The same* configuration then must, of course, be attributed to the three other salts here studied, as they evidently all are derived from the *dextrogyrotory triethylenediamine-ion* and they all have a circular dichroism of the same positive character²⁾.

But previously (§ 4; sub 2) and 2A) we have demonstrated that these salts (*L-cobaltum-*) have *the same* configurations as the *L-rhodium-salts* of the series; therefore, the *levogyrotory* $\{Rh(d-Chxn)_3\}Cl_3$ necessarily must have *the same absolute* configuration of its constituents as the salt: *L*- $\{Co(d-Chxn)_3\}Cl_3$ just mentioned. The *Rh-salt* is strongly *levogyrotory* and evidently, even after a suitable shift upwards, its dispersion-curve in the

1) W. KUHN and K. BEIN, Zeits. f. anorg. Chem., **216**, 323, 335 (1934); Zeits. f. phys. Chem., B. **24**, 335 (1934).

2) These salts, although accidentally *levogyrotory* in the red part of the spectrum and even in the greater part of the visible spectrum, must, therefore, more properly be designed as *D-salts* instead of *L-salts*. As we have, however, in our previous papers always denoted the *D-* or *L-*character with respect to the direction of the rotation of the complex in the *red* part of the spectrum, we here have preserved the old notation in order to prevent confusion.

whole visible part of the spectrum certainly still will remain below the zero-line, — just as in the case of the *levogyrotory triethylenediamine-rhodium-chloride*¹⁾, which as we formerly have stated, also has the same spatial

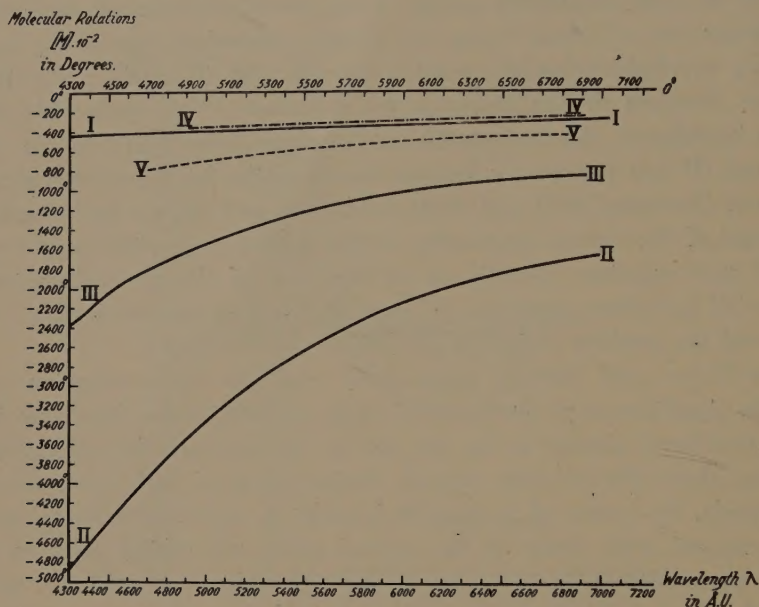


Fig. 4. Rotatory Dispersion of Levogyrotory Triethylenediamine(I), Tricyclopentanediamine(II), and Tricyclohexanediamine(III)-Rhodiumchlorides, all isolated from the least-soluble Cl- and Br--tartrates. IV is the curve for $L\text{-}\{Rh(\beta\text{-}2\text{-}4\text{-}Ph)_3\}Cl_3$; V that for $L\text{-}\{Rh(\alpha\text{-}meso\text{-}2\text{-}4\text{-}Ph)_3\}Cl_3$. (Ethylenediamine and $\alpha\text{-}meso\text{-}2\text{-}4\text{-}norm.$ Pentanediamine are non-resolvable; the salts of the two resolvable cyclic Diamines have the Constitution: $\{Rh(\alpha\text{-}Ept)_3\}Cl_3$ and $\{Rh(\alpha\text{-}Chan)_3\}Cl_3$ respectively. The curves I, II and III probably have all a flat minimum in the neighbourhood of 3000 Å.U. and evidently show a circular dichroism of negative character.

Fig. 4. Rotatory Dispersion of Different Rhodium-Salts.

configuration as the corresponding *dextrogyrotory cobaltic-salt*. From all these corollaries it follows, that also in the case of the *tricyclohexanediamine-salts*, the substitution of the central Co-atom by a Rh-atom and vice-versa must cause a reversion of the rotation of the complex itself which, in the red part of the spectrum, is only apparently hidden by the *levogyrotory* superimposed influence of the 3 *dextrogyrotory* molecules of the base introduced into it. Simultaneously it becomes clear, that here the solubility-rule of WERNER equally holds and that the disagreement mentioned in § 4 is only an apparent one, — conjured up, as it were, by the strong *levogyrotory* influence exerted by the three molecules of the *d*-base present in the complex *cobaltic-ion*. The *rhodium-salt*, it is true, has a circular dichroism (in the vicinity of 3000 Å.U.) of *negative* character; but the same occurs in the case of the *levogyrotory triethylenediamine-rhodium-salt*, which equally has the same spatial arrangement as the *dextrogyrotory*

¹⁾ Because it never can rise higher than the curve I, which corresponds to completely inactive basic molecules in the complex ion.

cobaltic-compound; and it is, therefore, evidently characteristic of *rhodium*-salts of this type. This negative COTTON-effect is actually co-ordinated with the fact, that all these *rhodium*-salts are *levogyrotory* in the *red* part of the spectrum. Most probably the absorption-band of the *rhodium*-salts in the ultraviolet really corresponds to that of the *cobaltic*-salts at about 4600—5300 A.U.; the *rhodium*-salts themselves are colourless¹⁾.

So far therefore, a perfect agreement exists between the deductions from WERNER's rule and from the other sources of information.

In the following paper we have to consider some facts concerning the *cyclopentanediamine*-salts in connection with the *triethylenediamine*-compounds, which, at first sight, seem to be in partial contradiction with the phenomena here discussed.

SUMMARY.

1. By means of the method of the optically-active racemates the validity of WERNER's solubility-rule was demonstrated as well in the case of the *triethylenediamine*-, as of the *tricyclohexanediamine*-salts of *cobaltum* and *rhodium*. The only apparent disagreement in the case of $L\{-\text{Co}(d\text{-Chxn})_3\}\text{Cl}_3$ was explained as certainly being caused by the superimposed action of the optically-active base present in the complex. The salts isolated from the least-soluble *chloro*- or *bromo-d-tartrates* all possess the spatial configuration characteristic of the *dextrogyrotory triethylenediamine*-ion.

2. As well in the case of the *triethylenediamine*-, as in that of the *tricyclohexanediamine*-salts the substitution of the central Co-atom by a Rh-atom not only causes a change of the magnitude, but simultaneously a *reversion* of the algebraic sign of the rotation of the complex, when that substitution occurs in ions with the same absolute spatial configuration.

¹⁾ According to I. LIFSCHITZ and E. ROSENBOHM (Zeits. f. phys. Chem., **97**, 1, (1920); Zeits. f. wiss. Photogr. etc., **19**, 198 (1920)) the *triethylenediamine-cobaltic*-salts have absorptionbands at about 4550 A.U., at 3390 A.U. and in the ultraviolet; those of *rhodium* at about 3000 A.U. and 2600 A.U., but not in the visible part of the spectrum.

*Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.*

Chemistry. — *Investigations on Complex Salts of racemic and optically-active Cyclohexane-1-2-diamines with Trivalent Cobaltum and Rhodium. I. On trans-Cyclohexane-1-2-diamine and its Fission into optically-active Antipodes.* By F. M. JAEGER and L. BIJKERK.

(Communicated at the meeting of December 19, 1936).

§ 1. The quantity of 1-2-diamino-cyclohexane necessary for the investigations on complex salts was obtained in the way previously described¹⁾: starting with pure cyclohexanone, first the cyclohexanone-oxalylester and then the corresponding cyclohexanone-carboxylic-ester of boilingpoint: 105°—106°.5 C. (under 12 mm. pressure) were prepared; the yield of the latter varied between 42—52 % of the theoretically expected quantity. Some cyclohexanone-oxalylic-acid of the meltingpoint: 122° C. was, as a by-product, obtained in beautiful crystals²⁾. The carboxylic ester was transformed into cyclohexane-dion-monoxime; the latter proved to be a viscous liquid, which could not be obtained in the crystalline state. The yield of it was about 86—87 % of the theoretical one. By means of hydroxylamine, the monoxime was transformed into the solid dioxime, which can readily be recrystallised from water and which has a meltingpoint of 187—189° C.

Cyclohexane-1-2-diondioxime crystallizes from water on slow evaporation in small colourless crystals with very lustrous faces and perfectly constant angular values. They are rhombic-bipyramidal, with:

$$a : b : c = 1.4938 : 1 : 0.9283.$$

Forms observed: $m = \{110\}$, predominant, highly lustrous; $a = \{100\}$, narrower than m , yielding good reflections, like the much narrower form $b = \{010\}$; $o = \{111\}$, well developed and giving very sharp reflections; $q = \{021\}$, well reflecting, often absent, the occurrence of $\{001\}$ as a limiting form is dubious. The habitus of the crystals is that of prismatic needles, flattened parallel to two faces of m . The crystals from acetone which are rudimentarily developed ordinarily are tables parallel to $\{001\}$ or to two faces of $\{111\}$, with m predominant, b well developed, q small; moreover, $c = \{001\}$ or two planes of $\{111\}$, only rudimentary and badly reflecting; $\{100\}$ is altogether absent in this case. (Fig. 1).

¹⁾ F. M. JAEGER and J. A. VAN DIJK, Proc. Royal Acad. Amsterdam, **39**, 384, 392 (1936).

²⁾ Ibidem, loco cit. p. 391.

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) =$	$56^{\circ} 12'$	—
$m : o = (110) : (111) =$	$41 \quad 50$	—
$b : o = (010) : (111) =$	$51 \quad 46$	$51^{\circ} 44\frac{3}{4}'$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$96 \quad 20$	$96 \quad 20$
$b : m = (010) : (110) =$	$33 \quad 48$	$33 \quad 48$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$76 \quad 28$	$76 \quad 30\frac{1}{2}$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$48 \quad 56$	$48 \quad 58$
$b : q = (010) : (021) =$	$28 \quad 27$	$28 \quad 18\frac{1}{2}$

Normal extinction on m , a and b . The plane of the optical axes is $\{001\}$.

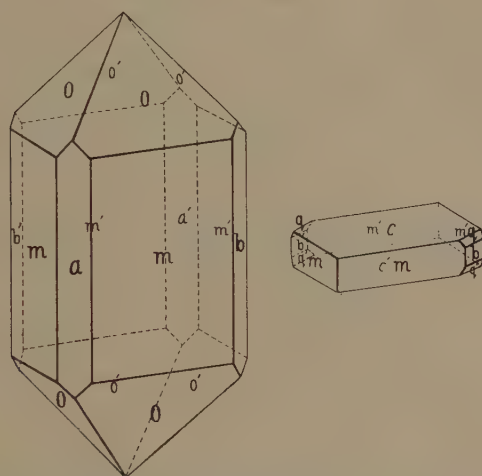


Fig. 1. Crystal form of Cyclohexane-1-2-dion-dioxime.

The compound forms complex *nickel*-salts which are characterized by their beautiful, deep violet-red colour. This *dioxime* was finally reduced by means of an excess of sodium and absolute alcohol in the way previously described; the different bases generated in this process were isolated in the form of their hydrochlorides and subsequently set free from those by means of caustic potash. The liquid mixture, after having carefully been dried over potassiumhydroxide and metallic sodium, then was subjected to a fractionated vacuum-distillation. Three different fractions could be isolated:

The first fraction yields a colourless base, which boils at 37°C . under a pressure of 15 mm. and at 134° — 135°C . under the ordinary pressure. This substance proved to be *monobasic*; it is the *mono-amino-cyclohexane*: $\text{C}_6\text{H}_{11} \cdot \text{NH}_2$ and forms a *benzoyl*-derivative, which melts at 146° — 147°C .

The second fraction consists of the *diamino-cyclohexane* itself; this base boils at 80° — 82°C . under a pressure of 12 mm. and melts at $14^{\circ} \cdot 8 \text{C}$. With *benzoylsulfochloride* it forms a derivative melting at 153° — 155°C .

The third fraction boiled at 100° — 105° C. under 12 mm. pressure: it unexpectedly, however, did *not* consist of the *phenazine*-base already previously isolated by WALLACH¹). The substance readily crystallizes from a number of organic solvents and also very beautifully from water. We found a meltingpoint considerably higher than that of WALLACH's base: 138° C., in stead of 106° — 108° C., as mentioned by this author. Its analysis yielded the following results: C: 74.05 %; H: 11.32 %; N: 14.31 %; calculated for $C_{12}H_{22}N_2$: 74.2 % C; 11.34 % H and 14.43 % N. The base: a *tetradecahydrophenazine* is identical with the α -*bistetramethylenepiperazine* described by GODCHOT and MOUSSERON²). It crystallizes from water with $1 H_2O$, which *cannot* be removed in vacuo, but only by dissolving the substance in anhydrous ether and thoroughly drying the solution over metallic sodium. It is very volatile, sublimes rapidly and can be distilled with water-vapour. The meltingpoint of 132° C. mentioned by the French authors is that of the *hydrate*; the *anhydrous* base melts at 137° — 138° C. The *hydrochloride* crystallizes with $3 H_2O$; analysis yields: 16.82 % H_2O ; 8.57 % N and 22.14 % Cl; calculated: 16.82 % H_2O ; 22.12 % Cl and 8.72 % N.

The *hydrochloride*: $C_{12}H_{22}N_2 \cdot 2HCl + 3H_2O$, crystallizes from its aqueous solutions on slow evaporation in small, thin, hexagonally-bordered tables, which are semi-transparent and have a mother-of-pearl-like luster. The crystals are *rhombic-bipyramidal*, with $a : b : c = 2.115 : 1 : 0.782$.

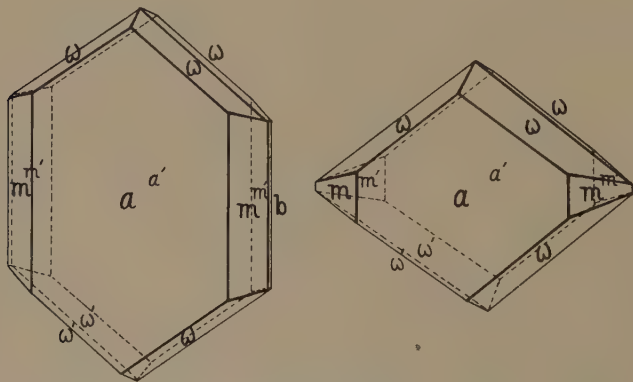


Fig. 2. Crystalform of α -Bistetramethylenepiperazine-hydrochloride ($+ 3H_2O$).

Forms observed: $a = \{100\}$, predominant, finely vertically-striated; $\omega = \{111\}$, about as broad as $m = \{210\}$; but more lustrous than the latter

¹) O. WALLACH, Lieb. Ann. d. Chem., **437**, 177 (1924): the dioxime was here reduced by means of KOH and Zn. Although the properties of this base are in some respects comparable with those of our base, the two substances yet were proved to be quite different ones.

²) M. GODCHOT and M. MOUSSERON, Compt. rend. Paris, **190**, 442 (1930); Bull. Soc. Chim., (4), **51**, 360 (1932).

form; $b = \{010\}$, very narrow, often absent. The habitus is thinly-tabular parallel to $\{100\}$:

Angular Values:	Observed:	Calculated:
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	$^{\circ}72^{\circ} 24'$	—
$a : \omega = (100) : (111) =$	$^{\circ}73 \ 47$	—
$a : m = (100) : (210) =$	46 44	$46^{\circ} 36'$
$m : \omega = (110) : (111) =$	51 23	51 $36\frac{1}{2}$
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	32 26	32 26
$\omega : \omega = (111) : (11\bar{1}) =$	98 20	98 25

The crystals are perfectly cleavable parallel to $\{100\}$.

The plane of the optical axes is $\{001\}$, with the a -axis as the first bissectrix. The double refraction is negative. The apparent angle of the optical axes is rather small; but the dispersion is very strong. Probably the axial planes for violet and yellow are perpendicular to each other.

From the higher boiling fraction (about 100° C. under 14 mm. pressure)

also a very small quantity of a *hydrochloride* was obtained, which from an aqueous solution containing an excess of hydrochloric acid crystallizes in small, apparently trigonal pyramids. In reality they prove to be rhombic bisphenoids, truncated by small faces of a prism. (Fig. 3).

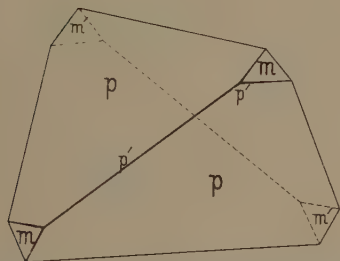


Fig. 3. Crystalform of *L*-Cyclohexanediamine-hydrochloride.

The crystals are anhydrous; analysis yielded: 37.81 % Cl; 14.27 % N; calculated: 37.97 % Cl and 14.9 % N.

Although the nitrogen-value is too low, there is no doubt as to the substance being the hydrochloride of the base mentioned.

Rhombic-bisphenoidal. Axial ratio: $a : b : c = 0.6831 : 1 : 0.7935$.

Forms observed: $p = \{1\bar{1}\bar{1}\}$, predominant, lustrous, but often yielding somewhat oscillating angular values; $m = \{110\}$, much smaller than p , but giving splendid reflections.

Angular Values:	Observed:	Calculated:
$m : m = (110) : (\bar{1}\bar{1}\bar{0}) =$	$^{\circ}68^{\circ} 35'$	—
$m : p = (1\bar{1}\bar{0}) : (\bar{1}\bar{1}\bar{1}) =$	$^{\circ}54 \ 42$	—
$p : p = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	109 24	$109^{\circ} 24'$
$m : p = (110) : (\bar{1}\bar{1}\bar{1}) =$	73 1	72 $45\frac{1}{2}$
$p : p = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	95 30	95 24

No distinct cleavability could be stated.

It is quite inconceivable in what way the crystals of this antipode have been formed. Originally we thought that the hydrochloride perhaps would manifest the phenomenon of a fission by spontaneous crystallization. For this reason the solubilities as well of the racemic as of the optically-active base were gravimetrically determined between 20° and 34° C.

Solubility of racemic and optically-active Cyclohexanediamine-hydrochlorides.				
Temperature <i>t</i> in °C	Grammes of the Salt in 100 Gr. of the Solution:		Grammes of the Salt in 100 Gr. of the Solute:	
	Racemic:	Opt. active:	Racemic:	Opt. active:
20°	45.35	46.72	82.99	87.69
26.1	46.41	47.54	86.60	90.62
30	47.14	48.17	89.19	92.94
33.7	47.86	48.70	91.78	94.93

From this follows that the racemic salt, being the more stable one, is less soluble than the optically-active; moreover, from the course of the solubility-lines it is seen that *no* intersection of them takes place at the ordinary and even much higher temperatures. The occurrence of a spontaneous fission, therefore, seems highly improbable.

The total yield of the racemic *cyclohexane-1-2-diamine* thus prepared (630 Gr.), calculated with respect to the quantity of the cyclohexanone used, does not exceed 23 % of the theoretically expected quantity.

§ 2. The base obtained possesses the *trans*-configuration, as is proved by its resolvability into optically-active components. This fission was performed by means of *d*-tartaric acid, — just as in the case of *1-2-diamino-cyclopentane*¹⁾. Whilst in the latter case, however, the *acid d-tartrates* proved to be most suited for this purpose, here we got better results by using the *neutral d-tartrates*. If the inactive base be combined with the calculated quantity of *d*-tartaric acid, the neutral *d-tartrate* of the *levorotatory* component for the greater part immediately falls out. After recrystallisation and fractionating, easily fractions are obtained with a specific rotation for sodiumlight of 11°, from which the pure lefthanded base can be separated, which has a specific rotation $[\alpha]_D$ of —36° and a boilingpoint of 82° C. under a pressure of 14 mm. At ordinary temperatures the base readily crystallizes and then has a meltingpoint of 42°.7 C.

Because the inactive base melts at 14°.8 C., the latter remains liquid at room-temperature. It is not possible to isolate the *dextrogyratory* component in a pure state from the mother-liquor of the *d-tartrates*, because, on evaporation, the solution gradually assumes the consistency of a glassy

¹⁾ F. M. JAEGER and H. B. BLUMENDAL, *Zeits. f. anorg. Chem.*, **175**, 161 (1928).

mass, without the very soluble tartrate separating from it. By fractional precipitation by means of absolute alcohol, a considerable quantity of the dextrogyratory component, could, however, be obtained, the latter showing a specific rotation $[\alpha]_D$ of 32° — 34° .

Therefore, the remaining *d*-component was isolated in still another way: to the concentrated mother-liquor now so much *d*-tartaric acid was added, as necessary to form the bitartrate. Soon a white precipitate appears, which has a specific rotation of about $+27^\circ$ and from which the dextrogyratory base can be obtained, showing an only slightly weaker positive rotation, than the negative one of the lefthanded component.

§ 3. The hydrochloride of *rac. Cyclohexanediamine* is highly soluble and usually crystallizes from its mother-liquors in featherlike aggregations of only approximately measurable crystals. Sometimes the hydrochloride is deposited from its aqueous solutions in rather poorly developed, long needles, ordinarily united in cross-shaped aggregations. The angular values are strongly oscillating, more especially in the zone of the prism, so that only approximate measurements can be made. *Monoclinic-prismatic*, with the axial ratio:

$$a:b:c=1.061:1:0.895 \text{ and } \beta=78^\circ 44'.$$

Forms observed: $m=\{110\}$, large, but with curved planes and yielding multiple reflections; $q=\{011\}$, small, well measurable; sometimes $c=\{001\}$, very narrow. The habitus is prismatic parallel to the *c*-axis. (Fig. 4).

Fig. 4. Crystalform of *rac. Cyclohexanediamine-hydrochloride*.

Most of the crystals are crossing twins, with $\{\bar{1}01\}$ as the twinning plane.

Angular Values:	Observed:	Calculated:
$m:m=(110):(\bar{1}10)=$	$^*87^\circ 42'$	—
$q:q=(011):(0\bar{1}1)=$	$^*82 \quad 28$	—
$q:m=(011):(110)=$	$^*54 \quad 45$	—
$q:m=(011):(\bar{1}10)=$	$67 \quad 54$	$68^\circ \quad 4'$
$c:q=(011):(0\bar{1}1)=$	$41 \quad 14$	$41 \quad 14$

No distinct cleavability was observed.

On $\{110\}$ oblique extinction, under about 14° with the direction of the vertical axis.

The plane of the optical axes is perpendicular to $\{010\}$, with the *b*-axis as the first bissectrix of negative character. On $\{110\}$ one axis is visible; there is a very strong crossed dispersion, the orange and blue colours being

visible in adjacent quadrants; for red the axial plane is almost parallel to $\{001\}$.

§ 4. The corresponding *nitrate*, on the other hand, is much less soluble than the hydrochloride and can easily be obtained in clear, colourless crystals.

They are *anhydrous*, as was proved by their analysis.

Racemic *Cyclohexanediamine-nitrate*: $C_6H_{10}(NH_2)_2$, $2HNO_3$ crystallizes from its acid aqueous solutions in beautiful, colourless, kite-shaped crystals.

Rhombic-bipyramidal: $a:b:c=0.9110:1:1.0612$.

Forms observed: $c=\{001\}$, well developed, very lustrous; $o=\{111\}$, large, yielding good reflections. The habitus is thick-tabular parallel to $\{001\}$. (Fig. 5).

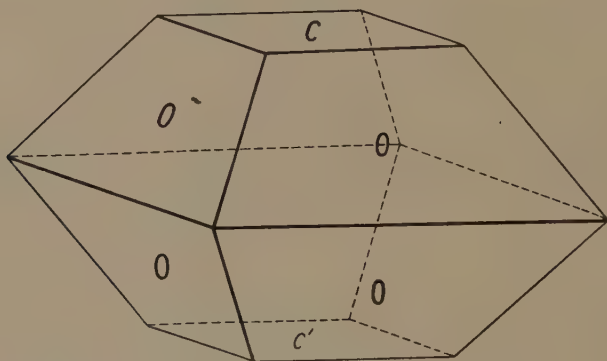


Fig. 5. Crystalform of *r*-Cyclohexanediamine-nitrate.

Angular Values:	Observed:	Calculated:
$c:o=\{001\}:\{111\}=$	$57^\circ 36'$	—
$o:o=\{111\}:\{\bar{1}\bar{1}\bar{1}\}=$	$77^\circ 14'$	—
$o:o=\{111\}:\{1\bar{1}\bar{1}\}=$	$68^\circ 58'$	$69^\circ 19'$

No distinct cleavability was observed.

Optically biaxial. The axial plane is parallel to $\{100\}$; the c -axis is the first bisectrix of negative character. On $\{001\}$ a rather large apparent axial angle is observed; rhombic dispersion, with $\rho > \nu$.

§ 5. The Optically-active Components.

I. The *hydrochloride* of the *dextrogyratory cyclohexanediamine* crystallizes from its hydrochloric acid containing or pure aqueous solutions in beautiful, colourless and highly lustrous crystals. They are *rhombic-bisphenoidal* with the axial ratio: $a:b:c=0.6831:1:0.7935$.

Forms observed: $q=\{011\}$, predominant; $o=\{111\}$, large and very lustrous; $p=\{1\bar{1}\bar{1}\}$, very small, well reflecting; $c=\{001\}$, narrow, but

well measurable. The habitus is prismatic parallel to the a -axis, usually somewhat flattened parallel to two opposite faces of q . (Fig. 6).

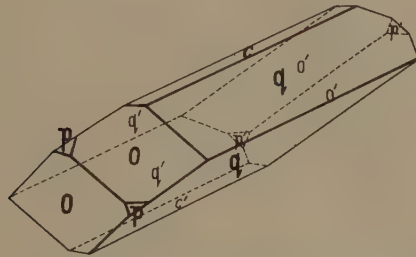


Fig. 6. Crystalform of *d*-Cyclohexanediamine-hydrochloride.

Angular Values:	Observed:	Calculated:
$q : o = (011) : (111) =$	$42^{\circ} 18'$	—
$c : q = (010) : (011) =$	$38 \quad 26$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$95 \quad 24$	$95^{\circ} 24'$
$q : q = (011) : (01\bar{1}) =$	$103 \quad 8$	$103 \quad 28$
$q : o = (0\bar{1}\bar{1}) : (111) =$	$80 \quad 25$	$80 \quad 19\frac{1}{2}$
$c : o = (001) : (111) =$	$54 \quad 42$	$51 \quad 35\frac{1}{2}$
$a : o = (100) : (111) =$	—	$47 \quad 42$
$b : o = (010) : (111) =$	—	$62 \quad 38$

No distinct cleavability was observed.

The plane of the optical axes is $\{100\}$; on $\{011\}$ and $\{0\bar{1}\bar{1}\}$ one of the axes is visible excentrically. Probably the first bisectrix is parallel to the c -axis.

II. The *hydrochloride* of the *levogyrotory* base shows the same angular values as the previous crystals, but here $p = \{\bar{1}\bar{1}\bar{1}\}$ is predominant and $o = \{111\}$ very small. Moreover, the form $m = \{110\}$ is here observed, small but very lustrous. The habitus (Fig. 7) is analogous to that of the

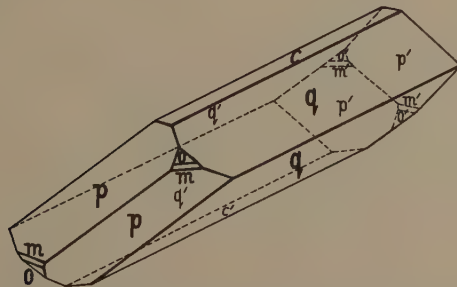


Fig. 7. Crystalform of *l*-Cyclohexanediamine-hydrochloride.

dextrogyratory salt or, — as formerly (Fig. 3) was described, to that of the bisphenoid p , truncated by small faces of m .

Besides the angular values previously mentioned, also the following angles were measured:

$$\begin{array}{lll} m : m = (110) : (\bar{1}\bar{1}0) = & 68^\circ 35' & 68^\circ 40\frac{1}{2}' \\ p : p = (11\bar{1}) : (\bar{1}\bar{1}1) = & 109 \quad 24 & 109 \quad 11 \\ m : p = (110) : (\bar{1}\bar{1}1) = & 73 \quad 0 & 72 \quad 45\frac{1}{2}' \end{array}$$

The optical orientation is the same as in the case of the other compound. The two kinds of crystals are perfect mirror-images of each-other.

§ 6. The optically-active *nitrates* are less soluble than the hydrochlorides.

I. The *nitrate* of the *dextrogyratory* base crystallizes from dilute nitric acid in colourless, well built, lustrous crystals. They are anhydrous.

Rhombic-bisphenoidal:

$$a : b : c = 0.9620 : 1 : 0.4725.$$

Forms observed: $o = \{111\}$ and $p = \{1\bar{1}1\}$, equally large and well reflecting; $m = \{110\}$, broad and lustrous; $a = \{100\}$, small but very lustrous; $\omega = \{2\bar{1}1\}$, very small, but well measurable; $r = \{101\}$, broader than $q = \{011\}$, both yielding feeble

Fig. 8. The Crystalform of *d*-Cyclohexanediamine-nitrate.

reflections; $n = \{120\}$, broader than r , well reflecting. The habitus (Fig. 8) is usually flattened parallel to two faces of $\{111\}$.

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) =$	$*43^\circ 53\frac{1}{2}'$	—
$m : o = (110) : (111) =$	$*55 \quad 43\frac{1}{2}$	—
$o : o = (111) : (\bar{1}\bar{1}1) =$	68 33	$68^\circ 33'$
$o : r = (111) : (101) =$	22 59	22 59
$o : p = (111) : (\bar{1}\bar{1}1) =$	45 58	45 58
$o : q = (111) : (011) =$	23 55	$23 \quad 56\frac{1}{2}$
$o : p = (111) : (\bar{1}\bar{1}1) =$	47 50	47 53
$a : o = (100) : (111) =$	66 5	$66 \quad 3\frac{1}{2}$
$m : n = (110) : (120) =$	18 33	18 39
$a : \omega = (100) : (2\bar{1}1) =$	48 18	$48 \quad 23\frac{1}{2}$
$p : \omega = (\bar{1}\bar{1}1) : (2\bar{1}1) =$	17 48	17 40

No distinct cleavability was observed.

The plane of the optical axes is $\{001\}$; an optical axis is visible on m almost perpendicular to the prism-faces. The a -axis, of positive character, is the first bissectrix. Strong rhombic dispersion with $\varrho > v$.

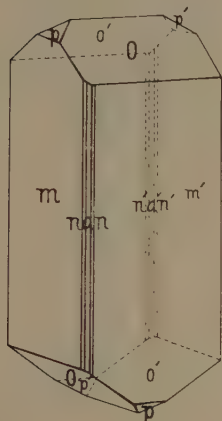


Fig. 9. The Crystalform of *l*-Cyclohexanediamine-nitrate.

II. The *nitrate* of the *levogyrotory* base is quite analogous to the former. Colourless, flat crystals, usually flattened parallel to two faces of $\{110\}$.

Rhombic-bisphenoidal:

$$a : b : c = 0.9539 : 1 : 0.4697.$$

Forms observed: $m = \{110\}$, broad and often yielding multiple reflections; $o = \{111\}$, large and lustrous; $p = \{111\}$, small, weak reflections; $a = \{100\}$, lustrous but narrow; $n = \{210\}$, broader than a and well reflecting (Fig. 9).

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) =$	$43^\circ 39'$	—
$m : o = (110) : (111) =$	$55 \quad 46$	—
$m : m = (110) : (1\bar{1}0) =$	$87 \quad 18$	$87^\circ 18'$
$m : p = (1\bar{1}0) : (1\bar{1}0) =$	$55 \quad 43$	$55 \quad 46$
$a : n = (100) : (210) =$	$25 \quad 38$	$25 \quad 30$
$n : m = (210) : (110) =$	$18 \quad 1$	$17 \quad 51$
$o : o = (111) : (1\bar{1}1) =$	$68 \quad 28$	$68 \quad 28$

The other physical properties are the same as in the case of the nitrate of the dextrogyrotory base.

§ 7. The rotatory dispersion of *d*- and *l*-Cyclohexanediamine.

As has already be mentioned, the optically-active antipodes of cyclohexanediamine, melting at $42^\circ.7$ C., are at ordinary temperature solid, well crystallized substances. As in aqueous solution, like the racemic base, they immediately form a strongly built *hydrate*, their rotation can only be exactly determined in the *molten* state. It may here be remarked that during our experiments with the complex salts derived from them, we more and more got the impression, that the "racemic" base actually is an equimolar *mixture* of the two antipodes and *not* a true chemical compound. The binary meltingpoint-curve, therefore, is most probably one with *two* branches, the meltingpoint of the inactive base ($14^\circ.8$ C.) being that of an *eutectic mixture*.

For the measurement of the optical rotation the molten base was enclosed

within a specially constructed polarimeter-tube (length: 19.87 cm.) which was surrounded by a wider mantle through which a steady current of the water from a thermostat was continually flowing at a carefully regulated rate. The temperature of the molten base thus was constantly held at 55° C.; the density of the liquid at that temperature was determined to be: 0.946. The tube was provided with the necessary diaphragms so as to screen-off, as completely as possible, the troublesome reflections of the light-rays at the walls of the rather thin tube.

In this way the following values of the rotation at different wave-lengths were determined:

Wavelength λ in Å.U.	Rotation 2α observed:	Specific Rotation [α]:	Molecular Rotation [M] . 10 ⁻² :
6480	—55.53	—29.47	—33.61
6262	—59.84	—31.77	—36.22
6074	—63.84	—33.90	—38.64
5893	—67.90	—36.05	—41.10
5735	—71.99	—38.22	—43.57
5592	—75.93	—40.31	—45.96
5463	—79.74	—42.34	—48.26
5340	—83.44	—44.30	—50.55
5224	—87.13	—46.26	—52.74
5126	—90.70	—48.15	—54.90
5036	—94.38	—50.11	—57.12
4950	—97.30	—51.66	—58.89

In Fig. 10 these values of [α] and of [M] . 10⁻² are represented in a graph (A and A'), simultaneously those of *cyclopentanediamine* (B and B') for the purpose of comparison¹⁾.

The *dextrogyratory* base which, as already mentioned, had a somewhat lower meltingpoint by the admixture of a small amount of the racemic one, showed rotations 2°—3° lower than the pure *levogyratory* base.

From these curves it is seen that as well the absolute magnitude of the rotation of the *cyclohexanediamine* for each wavelength, as the rotatory dispersion are less than for *cyclopentanediamine*. As we soon will see this phenomenon is in the same way revealed in the dispersion-curves of the

¹⁾ F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chem., 175, 168, 169 (1928).

colourless rhodium- and platinum-complexes derived from these optically-active bases.

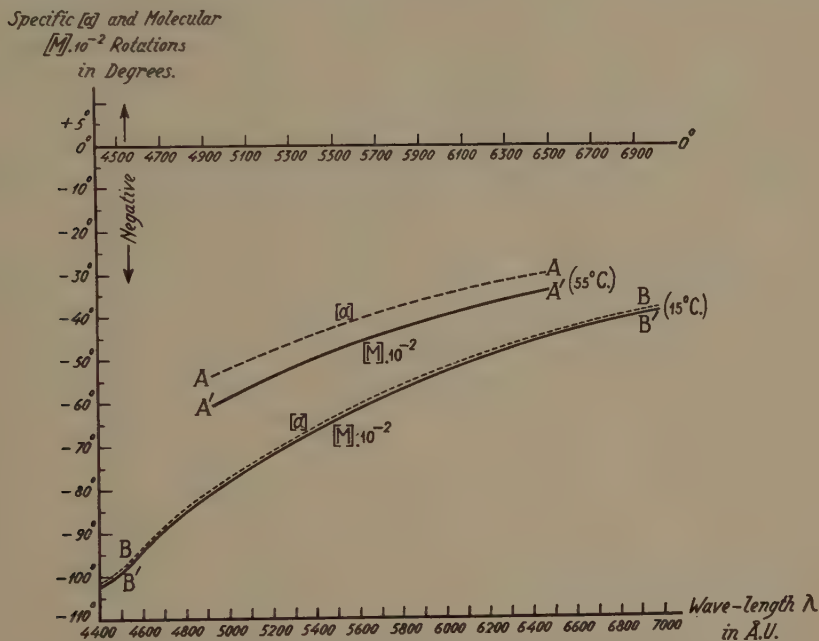


Fig. 10. The Rotatory Dispersion of the optically-active Cyclohexanediamines. (The curves B relate to the corresponding Cyclopentanediamines).

Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.

Chemistry. — Some properties of unsaturated sulphones. By J. BÖESEKEN and E. DE ROY VAN ZUYDEWIJN.

(Communicated at the meeting of November 28, 1936).

In a previous communication¹) one of us (B) pointed out that a saturated five-ring, exclusively consisting of carbon atoms, corresponds with regard to its properties with the analogous, non-cyclic saturated compound. This applied to the α -hydroxy-carbonic acids, where was stated by means of their behaviour towards boric acid that the ring closure did not alter the position of hydroxyl and carboxyl groups with respect to each other.

From measurements of the conductivity of mixtures of boric acid with cyclopentane-cis-hydroxy-carbonic acids²) it might even be concluded that in this ring there must still be some flexibility, allowing the adjacent

¹) Proc. Royal Acad. Amsterdam, **39**, 28 (1936).

²) J. BÖESEKEN, G. SLOOFF, J. M. HOEFFELMAN and H. E. HIRSCH, Recueil trav. chim. **52**, 881 (1933).

hydroxyl and carboxyl groups to deviate. It may be remarked here that CHR. VAN LOON³⁾ already in 1919 by comparing the behaviour of cis-cyclopentane diols, cis-hydrindene diol and pyrocatechol towards boric acid observed that "by the benzene ring the hydroxyl groups are pressed into one plane, so that a ring of five carbon atoms possesses a smaller degree of rigidity than is usually supposed".

If in the five-ring a double bond is present or if it is fixed to a benzene ring (CHR. V. LOON) or two five-rings have three C-atoms in common²⁾, the situation is changed, the flexibility has decreased, the derivatives must differ from the corresponding non-cyclic compounds or from the simple saturated ring systems respectively. This became apparent in the first place from boric-acid measurements and as far as unsaturated cyclic hydrocarbons are concerned from measurements of the velocity of reaction with peracetic acid, from which might be concluded that in cyclopentene a ring tension was present⁴⁾.

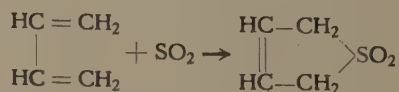
We now have asked what will be the result of the substitution of one of the C-atoms by another atom or another group of atoms.

It is a well-known fact that saturated five-rings with one atom of oxygen or of nitrogen display a great stability and the boric-acid measurements of the cis-diols derived from them show that conditions are found analogous to those of the corresponding cyclopentane diols.

We may point here to α -mannitan which causes a considerable increase of the conductivity of boric acid⁵⁾ and to N-ethyl antitartrimide, the influence of which is still somewhat larger⁵⁾.

Since we know now for certain that these increments are in direct connection with the position of the cis-placed groups in space, we may conclude that the substitution of one of the ring-forming atoms by another does not make an essential difference to the steric condition of the ring. The quantitative change points to a more rigid structure of these rings in comparison to the saturated ring which exclusively consists of C-atoms.

Sterically oxygen and nitrogen are situated close to carbon. Consequently it will be more interesting to examine substances in which one of the C-atoms has been substituted by a group, strongly deviating from the carbon and from the adjacent atoms in the natural system, both in mass and in nature. An opportunity to do this was offered by the discovery of a remarkable addition-reaction⁶⁾, that of SO₂ at the ends of a conjugated system:



³⁾ CHR. V. LOON, Thesis Delft 1919, p. 52.

⁴⁾ J. STUURMAN, Thesis Delft 1936. J. BÖESEKEN and J. STUURMAN, Proc. Royal Acad. Amsterdam, **39**, 3 (1936).

⁵⁾ Proc. Royal Acad. Amsterdam, **28**, 372 (1925). See also N. VERMAAS, Rec. trav. chim. **51**, 82 (1932).

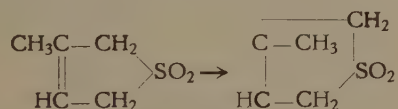
⁶⁾ EIGENBERGER, J. pract. Chem. [2] **127**, 307 (1930); **129**, 312; **131**, 289 (1931).

This addition-reaction takes place fairly quantitatively at room-temperature and is an example of the binding of a single atom to two atoms which in normal condition lie rather far apart in space. Since these generally well crystallizing cyclic compounds at a rise of temperature decompose into the two components, they may serve both for the quantitative determination of substances with a conjugated system and for their purification.

Moreover, from the easy decomposition it appears that a tension is present in this molecule, since in the saturated, not ring-shaped sulphones the C—S bond is exceedingly firm.

EIGENBERGER proved the composition of these cyclic sulphones; he found besides that in the presence of KOH by ultraviolet light they were changed into isomers.

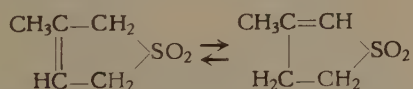
Owing to the fact that, on decomposition with metallic potassium, these isomers behaved in the same way as the original substances, he concluded that we have to deal here with a case of cis-trans isomerism:



On examination of the latter molecule in space, we see that very high tensions must be found in it, at any rate far higher than in the original molecule.

These isomers now happen to be much stabler than the original products, so that the configuration suggested by EIGENBERGER must be considered highly improbable.

A shifting of the double bond to the SO₂ group under the influence of the alkali seemed therefore much more likely.



Indeed, this structure has been proved by us by means of the ozonization-reaction, the isomerization thus being reduced to a conceivable shifting.

Considering that shifting of a double bond to an acidifying group under the influence of alkalis has been repeatedly stated, it was obvious that the alkali should be considered as the actual cause and *not* the light. The conversion indeed takes place also in the dark, only much more slowly; the ultraviolet light has exclusively an accelerating action.

At about the same time STRATING ⁷⁾ proved the structure of the isomeric cyclic sulphones, namely by application of the particular ozonization method found and described by us ⁸⁾.

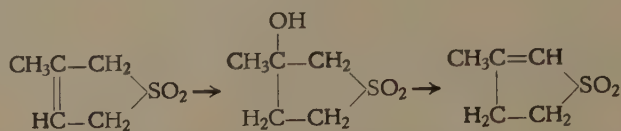
It was further found by STRATING and by us that, if the double bond of

⁷⁾ J. STRATING, Thesis Groningen 1934.

⁸⁾ Rec. trav. chim. **53**, 673 (1934).

the original sulphone no longer carried an H-atom, the conversion did not take place.

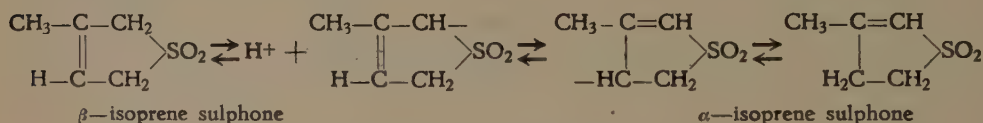
Since by the conversion always a hydrate was formed, BACKER and STRATING⁹⁾ thought that this should be regarded as an intermediate product:



in such a way that the OH group should be bound to the tertiary C-atom. On separation of H₂O, (possibly by the side of the original sulphone) the isomer should be formed, of which the position of the double bond, as stated above, had been established by their (and by our) researches.

If two alkyl groups were situated on either side of the double bond, the water molecule would be split off again in the same way.

We could prove that, under the conditions of the experiment, the hydrate remained unaltered, so that it may not be regarded as an intermediate product. The explanation should, therefore, rather be sought in the activation of an H-atom by the side of the SO₂ group¹⁰⁾, which then is split off as a proton, causing the formation of a negative ion. It has to be assumed here that the H-atom of the CH₂ group between the SO₂ and the C—CH₃ group is most easily activated and that subsequently the =CH group becomes the carrier of the electron; this takes up the proton again.



If there is no =CH group in the β -position, the proton returns to its old place.

Although objections may be raised to this theory, it is conceivable that it is a reversible process. We showed this, since the same final condition was obtained by starting both from the β - and from the α -isoprene sulphone. This was found by determination of the melting-point of the mixture which was ultimately obtained, after the melting-point curves of the two isomers had been determined.

At 30° this equilibrium lies at c. 91% of the α - and 9% of the β -sulphone. The equilibrium of the cyclic butadiene sulphones could not be determined in this way, since the formation of the hydrate (see above) made this impossible.

Yet, it could be stated qualitatively that we have to deal here also with

⁹⁾ Rec. trav. chim. **54**, 618 (1935).

¹⁰⁾ C. K. INGOLD and C. W. SHOPPEE, J. Chem. Soc. **1929**, 1199.

a reversible process, since the α -sulphone, derived from the β -sulphone, after complete purification, was again partly transformed into β -sulphone by means of alkali. After some time, on careful heating, butadiene and SO_2 were obtained, which is only possible if β -sulphone has been formed again.

We have further asked: is there any connection between this isomerization and the ring-structure? If this is not the case, non-cyclic β -unsaturated sulphones must also show this phenomenon. For this purpose we have synthetically constructed several of these compounds but, while hydration was stated, we observed nothing whatever of a shifting of the double bond.

This shows partly again that hydration is in no way connected with the shifting, partly that the unsaturated ring indeed exerts a pressure on the double bond in order to take a position which is more favourable to the stability.

That in these unsaturated cyclic sulphones a tension may be expected can be inferred from the steric conditions of such a ring-system, which correspond to those of the cyclopentenenes; the unknown factor lies here in the SO_2 group.

We thought that, in connection with STUURMAN's research (l.c.) on the velocity of oxidation of the cyclenes with peracetic acid, here also by means of a similar study from the values B and E in ARRHENIUS' relation:

$$\log K = -\frac{E}{2.303 RT} + B$$

a tension might be derived. However, the velocity of oxidation was exceedingly small (influence of the SO_2 group), but what was worse, irregularities were found which made it impossible to obtain any results in this way. Moreover, the supply of good comparable material for investigation met with great experimental difficulties.

For this reason we followed a more qualitative method. If it can be demonstrated that the saturated cyclic sulphone is less flexible than cyclopentane, it follows that in the unsaturated cyclic sulphone a tension occurs which is at least equal to that in cyclopentene. We tried to attain this by determination of the increase of conductivity of boric acid under influence of the *cis*-2.3 dihydroxy cyclosulphones.

The diols were prepared by oxidation of the unsaturated cyclic β -sulphones with KMnO_4 or $\text{KClO}_3 + \text{OsO}_4$, in which case indeed glycols were formed which increased the conductivity.

If this oxidation was performed with peracetic acid, the isomers were formed which were indifferent to boric acid.

From this result it appears that in case of the first method of oxidation the hydroxyl groups are placed on the same side of the ring, whereas with peracetic acid they come to be situated on either side. Consequently the very peculiar SO_2 group does not alter the steric course of these oxidations, an observation which highly raises the diagnostic value of these methods of oxidation for steric purposes.

Another remark may follow here. In oxidations with peracetic acid the primary oxidation product nearly always appears to be the oxide¹¹⁾. This oxide is formed by saponification with KOH of the mono-acetate of the diol obtained with peracetic acid, but can *not* be saponified into the diol by means of acetic acid. Here the very stable oxide is certainly not the intermediate product and the diol acetate must be the primary product¹²⁾.

Comparing the obtained increments of the conductivity with those of other ring systems (see table):

Increase of the conductivity of 0.5 m H_3BO_3 by some five-ring diols at 25°
(KOHLRAUSCH—HOLBORN $\times 10^{-6}$).

Diol	C	Δ	Observations
cis-butadiene sulphone 2.3 diol	0.5 m	+ 494	The isomers with transplaced hydroxyl groups do not exert a positive influence on the conductivity of boric acid.
cis-isoprene „ 2.3 diol	0.5 „	+1096	
cis-dimethyl butadiene sulphone 2.3 diol . . .	0.5 „	+1458	
ethylimide of anti-tartaric acid	0.2 „	+ 702	
α -mannitan	0.2 „	+ 772	
cis-cyclopentane diol 1.2	0.5 „	+ 149	
methyl 1 cis-cyclopentane diol 1.2	0.5 „	+ 114	
hydrindene diol 1.2	$\frac{1}{7}$ „	+ 63	

We see, taking into account the chosen concentrations, that the cyclic sulphonediols correspond more with the heterocyclic than with the isocyclic five-ring systems. With regard to what has been said in the introduction, it follows that the hydroxyl groups are more favourably situated to form complex boric-acid compounds.

This may have either a purely steric cause, a more rigid state of the five-ring, impeding the mobility of the hydroxyl groups, or an energetic one, brought about by the nature of the hetero-atoms in the ring.

Considering that the oxygen atom in the α -mannitan, the imid group in the tartrimid and the sulphone group in the cyclic sulphones, groups which differ so much in nature, exert an analogous influence on the formed complexes, it is obvious, of course also taking into consideration all other researches in this field, that mainly steric factors must be assumed. If we accept this supposition, the saturated sulphones will have a somewhat more rigid structure than the simple cyclopentanes, and the unsaturated cyclic sulphones will possess a considerable tension. Determination of the heat of combustion of these compounds and of their saturated hydration products would here undoubtedly give the desired explanation.

¹¹⁾ J. BÖSEKEN and G. C. C. SCHNEIDER, Journ. f. pr. Ch. N. F. **131**, 285 (1931).

¹²⁾ It is possible that first a labile oxide is formed.

Anatomy. — *The spread of primitive humanity and its links with the more differentiated races, as revealed by cephalic and cranial index curves.* By C. U. ARIËNS KAPPERS.

(Communicated at the meeting of December 19, 1936).

II. *The spread of 73—75—77(8)—80 cephalic index groups in Polynesia, America, Asia, the Arctic and Europe.*

Since the Polynesian islands, with the exception of the Sandwich group, are located on the same latitude as Melanesia and Australia, it is not strange that Indo-Melanesian and also "Australoid" elements are found on these islands, albeit sporadically and among the ancient population chiefly.

The curves¹⁾ of the male and female Maori skulls from New-Zealand (Table I fig. 1), have a distinct peak at 72. This opens the possibility of Australoid admixture, as also stated by MOLLISON, although among the male dolichocephalic skulls also the long-headed Indonesian type may occur. The Indonesian type, however, is most conspicuous by the high male cranial 76 peak.

Similarly the continuous and dotted curves of male cephalic indices of living Maori in Table I, fig. 4, show that among the present Maori both Indonesian cephalic index peaks, the 75 and 77 peak, occur²⁾.

With the male and female Moriori skulls from the Chatham islands (Table I fig. 2) the dolichocephalic peak fails, but the 76 peak is just as pronounced as with the Maori skulls, thus confirming TREGGAR's, DUCKWORTH's, DONNE's and ROSINSKI's opinion that the extinct Moriori probably were closely related to the Maori.

This cranial 76 peak also occurs in the male skull curve of the other Polynesian islands (Table I fig. 3) and may correspond with the cephalic 77 peak, indicated with the male Samoans (dotted line fig. 5) and especially with the male Marquesans (fig. 6). Besides the small 78 elevation in fig. 3 might correspond with the 80 cephalic groups, in figs. 5 and 7.

While our cranial curves compared with our cephalic curves of these Polynesian islands give evidence of a once quite numerous but now decreasing Nesiote element in these islands, the 80, 82 and 86 elevations in the male cranial curve of fig. 3, corresponding with 81, 83 and 86 cephalic peaks, already indicate Asiatic admixture and the cephalic 79, 81, 83, 85 and 86 indices so prevailing with the present population of the Tonga, the

¹⁾ In all my curves the index figure 70 stands for 70—70.9 etc.

²⁾ The 79 and 81 peaks in the dotted curve of fig. 4 suggest that the majority of this group (as the same peaks in fig. 6) is of Neo-Polynesian origin.

Marquesas and the Society islands (Table I figs. 5—9) clearly show the increase of this element, responsible for the different aspect of most of the present Polynesians compared with the population of Nesiote origin. Yet, the 75, 77 and 80 elevations in figs. 5, 6 and 7 confirm SULLIVAN's and BUCK's statement that on the above mentioned islands Nesiote elements still occur. SULLIVAN, who emphasized their Negroid character, found this type quite numerous on the Marquesas, which agrees with the high 77 elevation in fig. 6. It is conspicuous also among the Samoans (note the 77 and 80 peak in fig. 5).

In this connection it is interesting to note that the bloodtype of STEPHENSON's Samoans (Sam., Table 111) closely approaches that of BIJLMER's Ambonese and Halmaheira people, (Amb., Hal. and Sahu Hal.) and BROUWER's Alorese and Pantarese (Alor, Pant.) as well as HEYDON's and MURPHEY's New Guineans (N.G.) and KALTHOFEN's Kai Kai Papuans¹).

In the Sandwich islands, the Nesiote type is very rare nowadays. The cephalic curves of the male and female Hawaiians, registered in Table 1 figs. 10 and 11, strongly resemble the Malayan type, as appears from the curves of HAGEN's, KOCH's and BOK's male Javanese and KLEIWEG DE ZWAAN's Menangkabau Malays, added to these figures.

KEANE-QUIGGIN-HADDON also speak of two elements in the Polynesian people, distinguishing an older "Indonesian" and later "Malayan".

Indo-Melanesian (Nesiot) types in America.

TEN KATE considered the six ancient hyperdolichocephalic skulls found by him in the Mexican part of the Peninsula of California, some other authors also the skulls from the Southern Californian islands recorded by BOAS as Melanesian in character and origin.

Similarly RIVET emphasized the Melanesian character of SØREN HANSEN's ancient Lagoa Santa skulls of Brazil and of his own Ecuadorian Paltacalo skulls, as did SULLIVAN and HELLMAN for the Ecuadorian Punin skull (ind. 70, 96) and VERNEAU for some ancient Columbian skulls. The same is said of the Brazilian Botocudos, the Patagonians and Fuegians.

Cultural arguments for an early transpacific influence on America are numerous (cf. RIVET, FRIEDERICI²), KOHLBRUGGE³), DIXON⁴).

Recently HRDLICKA⁵) pointed out that the ancient South-American and

¹) The bloodtype of BIJLMER's Mimika Papuans from the South coast of New Guinea (Mim., Table 111) lies nearer some Australian (Aus.) bloodtypes (Mimika $r = 61.3$; $p = 28.7$; $q = 10$; North Australians $r = 66.2$; $p = 33.8$; $q = 0.0$, Burton Cleland) as also their cephalic indices do.

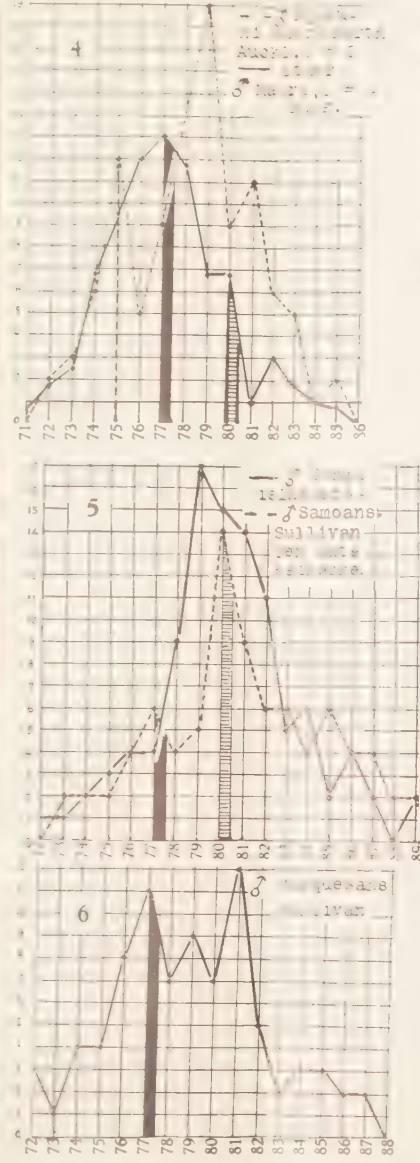
²) FRIEDERICI, Zu den vorkolombischen Verbindungen der Südseevölker mit Amerika Anthropos, Bnd. 24, 441 (1929).

³) KOHLBRUGGE, Systematisch en beschrijvend leerboek der Volkenkunde, 1930.

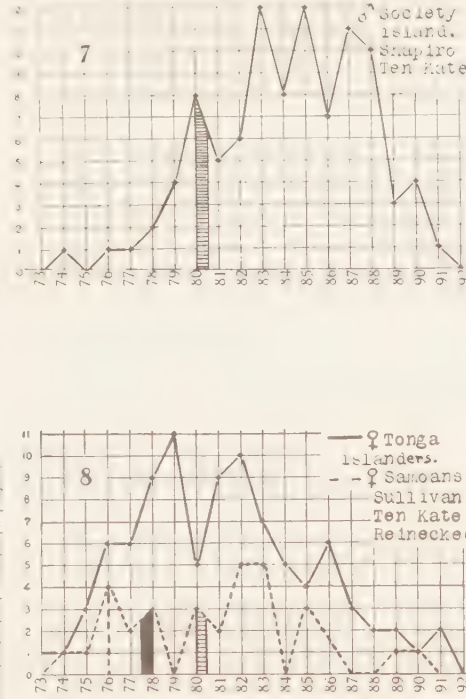
⁴) See: American aborigines, Toronto Press, 1933, p. 315.

⁵) Melanesians and Australians and the people of America, 1935.

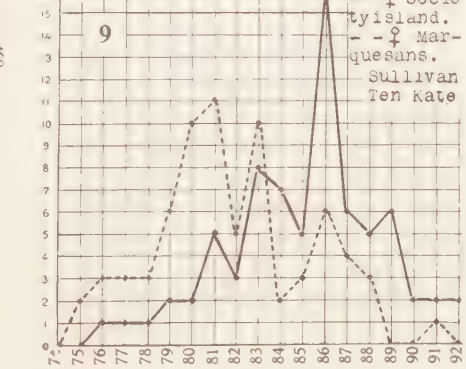
TABLE I POLYNESIANS
CRANIAL IND.



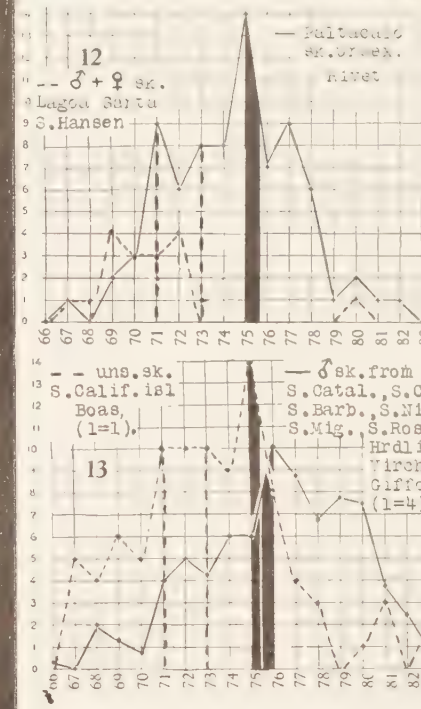
CEPHALIC INDICES



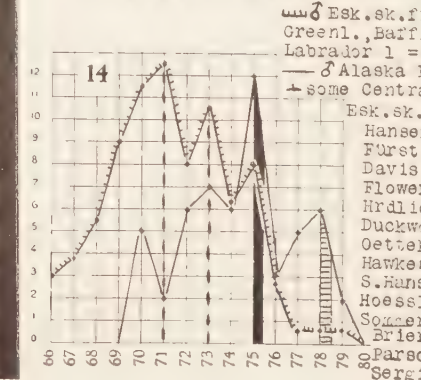
CEPHALIC INDICES



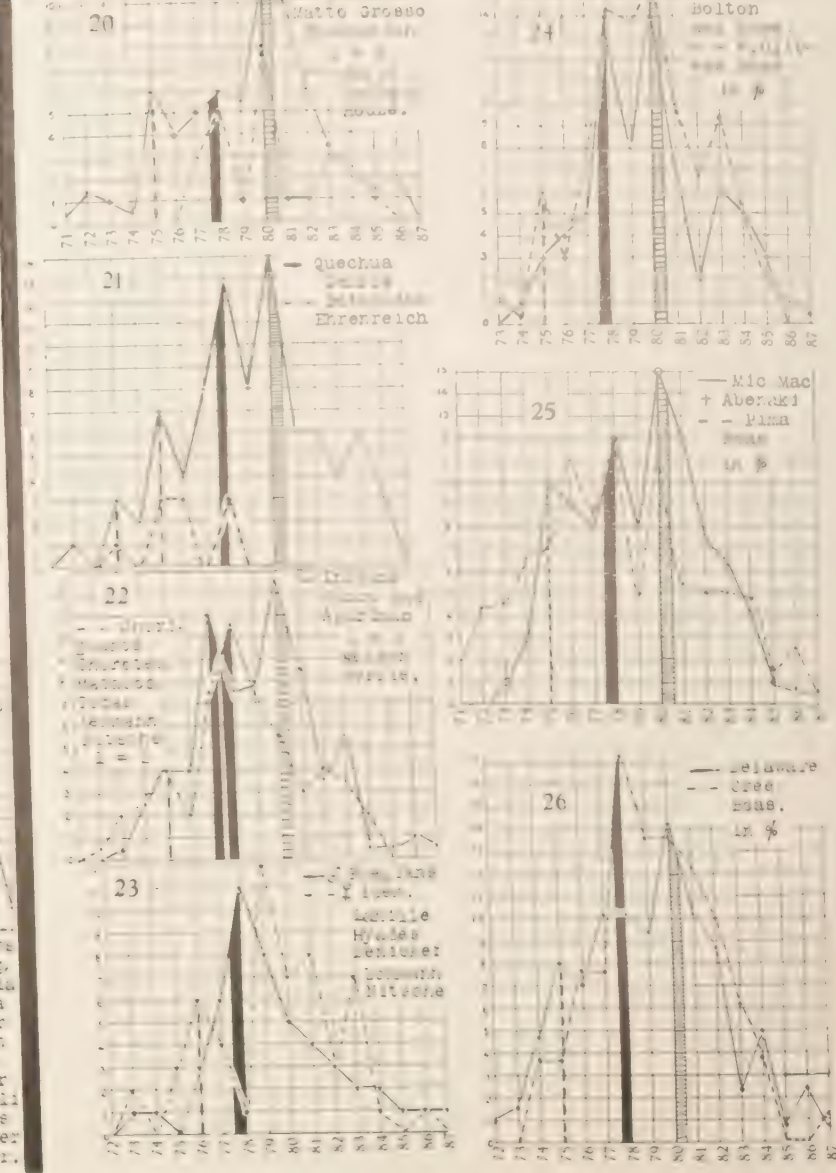
CRANIAL INDICES AND



ESKIMO SKULLS.



CEPHAL. IND SOUTH & NORTH AM. IND.



Californian skulls — in some respects — resemble also the Eskimo skulls and the more or less ancient Algonkin and Huron skulls from the North-Eastern States of N. America. Our curves confirm this view point for the l. br. index relations.

TEN KATE's Southern Californian skulls not being numerous enough to give a reliable curve, I registered in the dotted line of fig. 13 BOAS' unsexed ancient S. Californian skulls (in the continuous line HRDLICKA's, VIRCHOW's and GIFFORD's skulls) to compare them with RIVET's unsexed Paltacalo and HANSEN's Lagoa Santa skulls¹) (fig. 12) and with the male Eskimo skulls of fig. 14.

The continuous curve of figs. 12 and the dotted curve of fig. 13 resemble each other, the Paltacalo and BOAS' S. Californian skulls having in common a 71, 73 and a still higher 75 elevation, so frequently found also with the groups discussed in my preceding paper. The Lagoa Santa skulls (dotted line fig. 12) only correspond with the dolichocephalic skulls of BOAS' Southern Californian series, but the male Greenland Eskimo skulls again show elevations at 71, 73 and 75. I shall return to the Eskimoes later. First I shall refer to some other groups of skulls which give still more evident curves of the type in question. These groups are mostly South-American ones, especially from the Pacific side, but also from Brazil.

So the Botocudos skulls (fig. 15) give a high elevation at 73 and smaller ones at 71 and 76 reminding of the Indo-Melanesian curves published in our preceding paper.

A very characteristic Nesiote index combination is given by the male skulls from the Peruvian highlands recorded by MAC CURDY, specially by his male *Paucarchaucha* skulls, registered separately in the combed curve of fig. 16²). That several living groups in this part of S. America have corresponding cephalic peaks appears from figs. 20, 21 and 22 in which I registered EHRENREICH's Indians from the Matto Grosso and Amazonas (fig. 20), his Botocudos (fig. 21), HOUZÉ's Paria (fig. 20), the male Quechua recorded by FERRIS (fig. 21), the latter's and NELSON's Cuzco and Apurimac Indians and LEHMANN—NITSCHKE's Chiriguanas, Chorotes, Matacos and Tobas (fig. 22).

The Indo-Melanesian character is again very pronounced in the curves of the ancient male and female Patagonian skulls of the Rio Negro district (fig. 18) in which the (71-)/73- and 76 and 78 peaks, so characteristic of our Nesiote skull curves again are prominent, though brachycephalic (Araucanian?) admixtures are numerous.

The Fuegian skulls (fig. 19) show a purer Nesiote curve. GUSINDE and LEBZELTER considered the Fuegians as being Australoid. Our curve of male Fuegian skulls with its 73 and 76 peak, however, is very different

¹) I am greatly indebted to Prof. SØREN HANSEN, Copenhagen, for sending me the measurements of all the true Lagoa Santa skulls hitherto found.

²) LATCHAM's Chilean skulls (fig. 17), though more specialized, probably also belong to this category.

from the male Australian curve in fig. 25 on Table I of our preceding paper, and evidently suggests a relationship with our Indo-Melanesian or Nesiot group¹).

The 78 peak of the living male Fuegians (continuous line fig. 23) recorded by HYADES and DENIKER, LAHILLE and LEHMANN—NITSCHÉ equally suggests Indo-Melanesian relationship and so does the female 76 peak (dotted line same figure), occurring also with our female Indo-Melanesians (see our preceding paper Table I fig. 12).

All these curves make it possible and even probable that a people of the same stock as our Nesiot group — so widely spread also among the ancient Polynesians — is represented in South America and the fact that such curves chiefly occur with people from the Pacific coast favours this conception, strongly defended also by KOHLBRUGGE.

In connection with the problem of the origin of the North-American Indians it is worth while to note that similar cephalic curves are found also with several tribes of North-American Indians. So in the curve of the ancient skulls of the Mound dwellers of Ohio, published by BOAS, the 76 peak is by far the highest.

The cephalic curves of the Shoshoneans and Western Ojibwas (fig. 24), those of the Eastern Abenaki and Micmac Indians, of the Pima (fig. 25) and the Delaware and Cree Indians (fig. 26) show the 75—77(8)—80 peak combination. The indicial arrangement of these and several other North-American Indian tribes so closely resembles our Southern paleo-American groups that it raises the question if the theory of the immigration of the North-American Indians via the Aleutian and Behring Straits, which cannot have occurred earlier than at best 10000 years ago, should not be restricted to some tribes only, while others might have developed from more Southern paleo-American groups. For this also the uniformity of the South and North-American Indian bloodgroups and the great serological difference between the North-American Indian and Asiatic Mongolian type might be advanced (cf. Table III).

The Eskimoes.

As stated above, the cranial Eskimo curves (Table I fig. 14) fall in the same category with our paleo-American and other primitive groups. The blood type of the Greenland Eskimo²), however, though resembling the Indian blood type in having a small B, differs from it by a high A by which they closely approach the West Europeans and Australians (Table III).

¹) Also the indices of the female and unsexed Fuegian skulls (not registered in my table) are far too high to be Australian.

²) Only a small group of Eskimoes of Cape York (ESK. C. Y. Table III) falls in the category of the American Indians, all larger groups of Greenland Eskimoes stand nearer the Nordic European type. Also linguistically a sharp demarcation exists between the Eskimoes and North American Indians.

Undoubtedly the Eskimoes are offshoots of the same primitive stock, once widely spread along the shores of the Pacific and Atlantic.

This also appears from the fact that their index peaks show the same mutations. Whereas the total number of the male cephalic indices of Alaska Eskimoes registered in Table II fig. 9 (continuous line) shows a small 73, a higher 75(6) and a very high 78 elevation, the separately registered indices of HAWKES' male Eskimoes from Point Barrow, Herschel island and Behring straits have prevailing 73 and 75 peaks and only a small 78 elevation.

HAWKES' group comes nearer the cephalic indices of HANSEN's Eastern or Greenland Eskimoes (combed line same figure), the majority of which is dolichocephalic, as also appears from the curve of Greenland Eskimo skulls (combed line, Table I fig. 14) which has its highest elevations at 71 and 73 (corresponding with the 73 and 75 cephalic peaks). Contrarily the Alaska Eskimo skulls (continuous line, Table I, fig. 14) show a small 73, a high 75 and even an additional 78 peak.

Our Eskimo curves clearly show that the indicial relationship of the various Eskimo groups is of the same category as that between the other mesocephalic and dolichocephalic primitives.

It is difficult to say along which way or ways the Eskimoes reached the arctic regions. The facts appearing from UHLENBECK's¹⁾ studies concerning the Uralic and Indogerman elements in the Eskimo language may perhaps be interpreted as pointing to a Western Asiatic origin. UHLENBECK himself suggests the steppes of Northern and Central Asia. East-Asiatic affinities and migration via the Behring straits are supported by the similarity of paleo-Siberian (fig. 7 and 8) and Alaska Eskimo (fig. 9) curves and by the close resemblance between HAWKES' Eskimo and MONTANDON's male Ainu curve (fig. 6). Ethnological facts also plead for this, as does RUGGLES GATES' test of 16 Alaska Eskimoes²⁾.

The difference between the Eastern Asiatic blood type which as far as hitherto examined has a small A and large B, and the Greenland type with its large A and small B and the much closer approach of the Greenlanders to the Mediterraneo-Atlantic type (Table III) pleads for European admixture (RUGGLES GATES^{2a)}).

Yet the ancient character of A (compared with B) emphasized by RUGGLES GATES³⁾ suggests that this affinity may be also very ancient. For this the similarity of the Eskimo and Chancelade skull (MORANT) may be advanced. Since the Southern point of Greenland is several degrees more south than Iceland and lies on the same latitude as Oslo and the Farøe, this migration (like early historical migrations from Northern Europe) was quite possible, the more so as it was favoured by sea currents, also responsible for some zoological and botanical dispersions in this direction (SCHARFF).

¹⁾ UHLENBECK, Eskimo en Oer-Indogermaansch. Mededeel. der Kon. Akad. v. Wetensch., afd. Letterkunde Deel 77, 1936. I am greatly indebted to prof. UHLENBECK for several enlightening personal communications on this subject.

²⁾ RUGGLES GATES: Am. Journ. of phys. Anthr. Vol. 12, 1929, p. 475; 2a): Man, 1935 (36).

³⁾ Journ. of the Anthr. Inst. Vol. 64, 1934, p. 23 and Genetica Vol. 18, 1936, p. 47.

Asia.

Although the most evident representatives of our index type on the Asiatic continent are found in South-East Asia, some more northern groups of Asiatics, who otherwise show considerable differences with the southern primitives, probably may be considered as higher differentiations of the same primitive stock.

The spread of this index stock may be observed West, North and East of the Himalayas, i.e. in Beluchistan and Persia, on the Pamir plateau as well as in North-East and North Asia. To begin with Western Asia (Table II), it is striking to find analogous index relations with Indo-Aryan groups (fig. 1), with the Makhianis of Beluchistan (fig. 2), with the Persians from Ispahan, measured by the KRISCHNERS (fig. 3), the Kurds (combed line, fig. 4) and a group of Pamirese (continuous line same figure) and even with the Tibetans (fig. 5). Although these peoples differ from each other (the Pamirese and Tibetans have pronounced Mongoloid features) and especially from those dealt with in my preceding paper, the similarity of index peaks suggests that they are differentiated from an analogous stock. This is especially striking with the Ainou (fig. 6), whose primitive character has long been recognized.

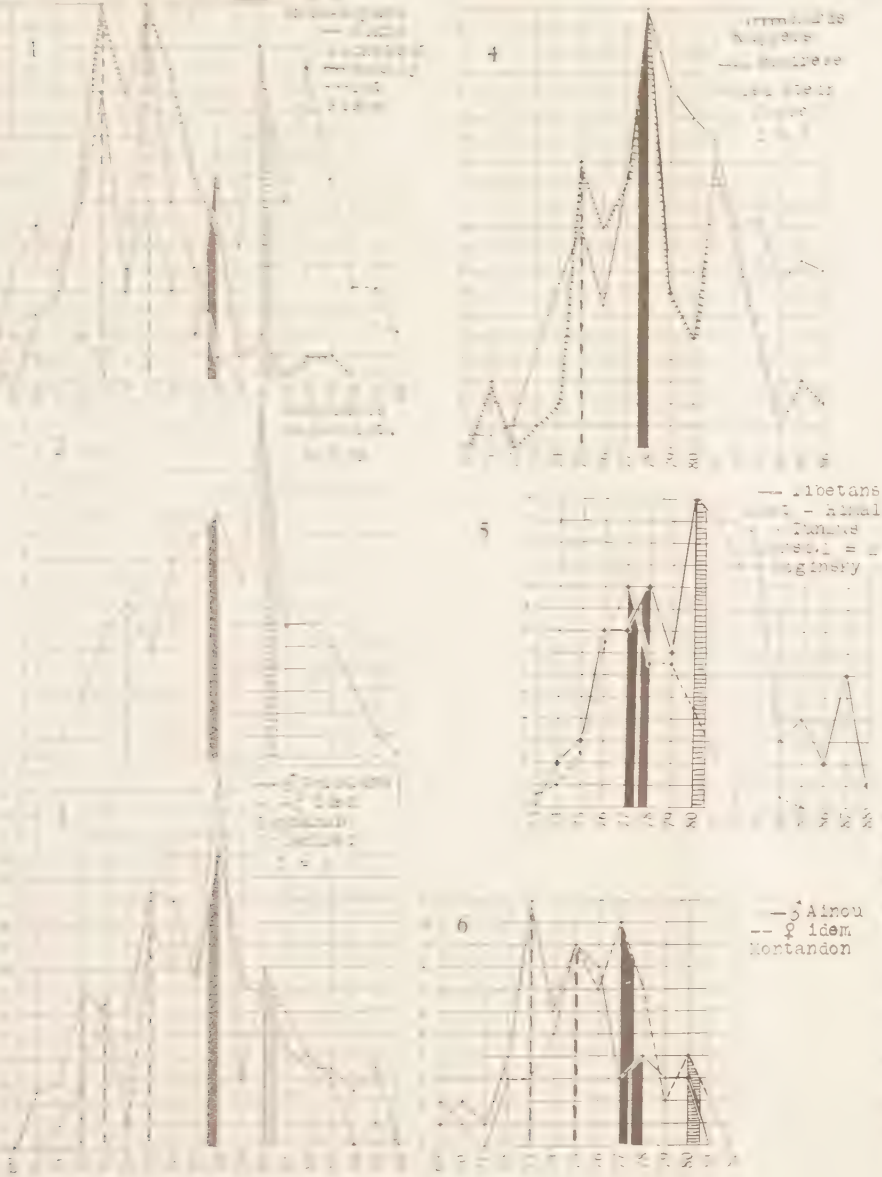
Also with several paleo-Siberian tribes related index curves occur. With SOMMIER's male Ob-Ostyaks (fig. 7) and with JOCHELSON—BRODSKY's male Tunguse and Yakughirs (fig. 8) the 78 peak is again combined with an 80 peak. Although these Mongoloid-looking peoples differ in many aspects from those mentioned before, the similarity of their index curves is very striking and once more shows the great constancy of this index type. Yet, as first proved by BOAS, the index is not unalterable. I have, however, shown that also its alterations follow a definite rule. For the group of indices we are now dealing with this rule is the possibility of transition of the cephalic 73—75 peak groups into 77(8)—80 groups.

Europe.

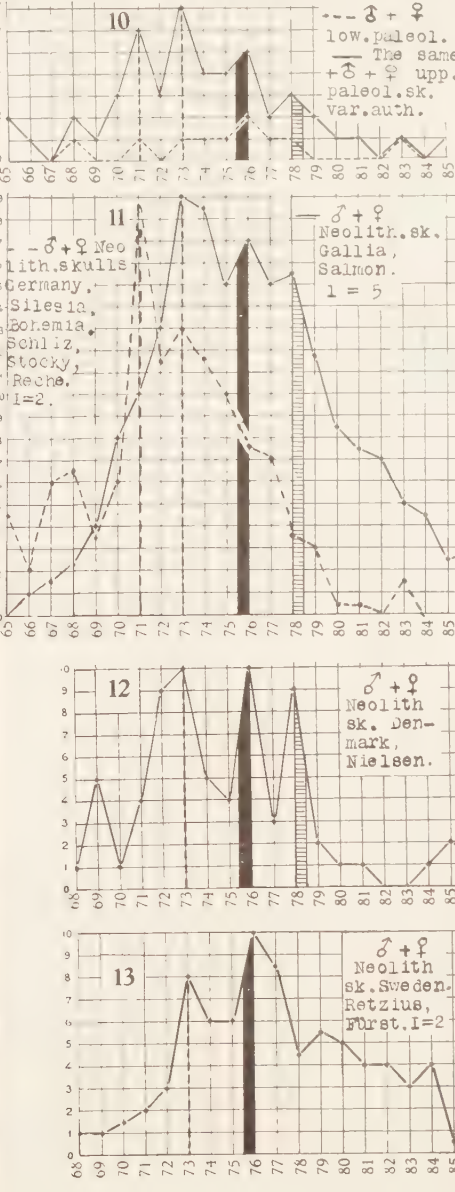
The relationship of the 73—75 and 78—80 peaks is not less evident in Europe viz. from both sides of the Mediterranean (Hamites and Mediterraneans proper) to the Atlantic coast. Besides, this index curve may be traced here from the earliest population of these regions up to our times, again showing an increase of the 78—80 cephalic (or 76—78 cranial) peaks in comparison to the 73—75 cephalic (or 71 and 73 cranial) peaks.

This is shown by comparing cranial curves of the paleolithic, neolithic and recent periods of Western Europe. In figs. 10—12 of Table II the constant occurrence of the 73, 76 and 78 peaks in our curves is very striking, but whereas the paleolithic curve (fig. 10) is still complicated by a pronounced 71 peak, while its 76 and especially its 78 peak are lower than the 71 and 73 peak, in the neolithic skull curve of France (fig. 11) the 71 index no more gives a special elevation and the number of 76 and

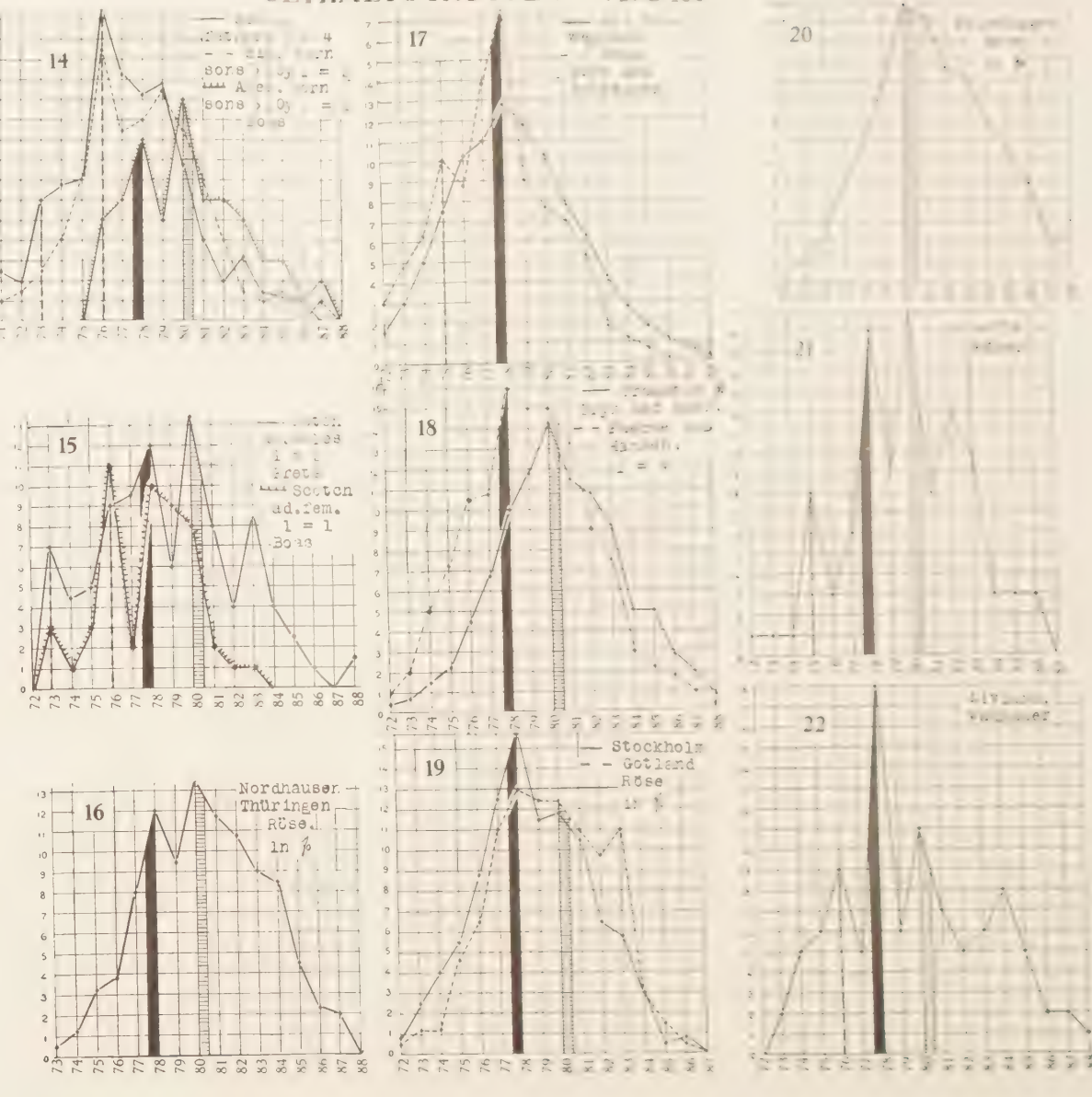
TABLE II CEPHALIC INDICES ASIA



CRANIAL INDICES WEUR.



CEPHALIC INDICES WEUR.



78 indices has relatively increased. In the neolithic Danish curve (fig. 12) the 76 and 78 peaks are about equally high as the 73 peak.

In the neolithic Swedish curve (fig. 13) the 78 index is not outstanding, but the 76 index is higher than the 73. We thus find a relative decrease of the 73 cranial index group especially in northern direction.

The spread of Mediterranean cromlech builders in northern direction along the Atlantic coast being a generally accepted fact, the gradual numerical change in the relative numbers of the skulls in question in northern direction to a prevailing meso-subbrachycephalic type might be advanced in favour of SERGI's opinion that the Nordics (better: Atlantics), notwithstanding their higher index have gradually developed out of Mediterranean groups before the arrival of the Central European Indo-Germans whose skull curve, (dashed line fig. 11) moreover shows far more dolichocephalic indices, and who probably had their cradle land in S. W. Asia, as I tried to prove elsewhere¹). That cephalic index peaks characteristic of Nordic races (78 and 80) may arise in a Mediterranean group by change of circumstances appears from BOAS' data concerning the Sicilian born and American born sons of Sicilian fathers (and mothers). In fig. 14 I again give the curves showing the prevailing Mediterranean (76) peak with the Sicilian born sons and the characteristic 78 and 80 peaks with the American born sons of the same age group and of the same parents²).

In favour of the conception that similar changes may have occurred in the development of our European Nordics (better Atlantics) figs. 15, 17, 21 and 22 may be advanced, showing that with several of our most typical North-European groups peaks of the more primitive 73 and 75(6) cephalic indices still occur in addition to the prevailing 78 and 80 peaks, the only ones in figs. 16, 18, 19 and 20.

While our figures show that analogous index curves occur with such different groups as Austronesians on the one hand and Mediterraneo-Atlantics on the other, thus decreasing the importance of the index curve as a radical distinction, they undoubtedly prove that there is a great tenacity in this curve and a definite system in its mutation.

Besides, our conclusion that there is a continuity between the Oceanian races from South America to Indonesia and Southern Asia and the Mediterraneo-Nordic races closely agrees with FROBENIUS' conclusion, based upon ethnographic data, especially upon the spread of sun-culture, traces of which are found in a paratropical girdle extending from America via the Pacific and Southern Asia to the Mediterranean and from here north along the Atlantic even beyond England, an ethnographic

¹) See *An Introduction to the Anthropology of the Near East in ancient and recent times*, Amsterdam, 1934, p. 94. See also HERMANN GÜNTERT: *Der Ursprung der Germanen*, Heidelberg, 1934, p. 62 and WAHLE: *Deutsche Vorzeit*, 1932.

²) GENNA's paper on the population of Trapani (1932) shows that also in this Sicilian town the 78—80 peak type prevails.

continuity confirmed by KOHLBRUGGE on account of the spread of megalolithic monuments.

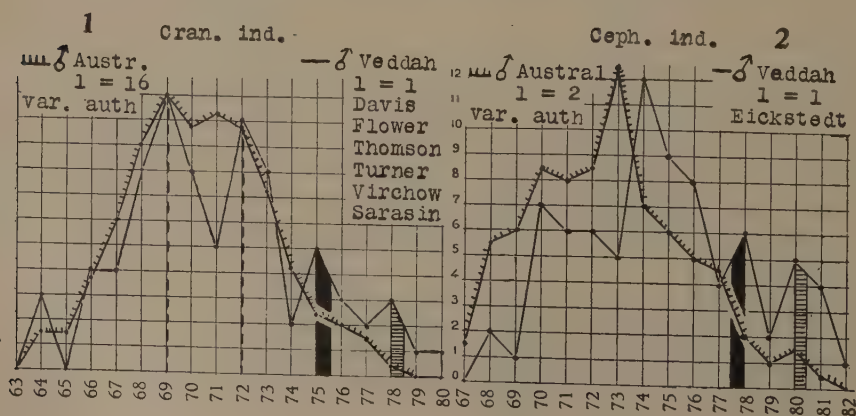
Discussion.

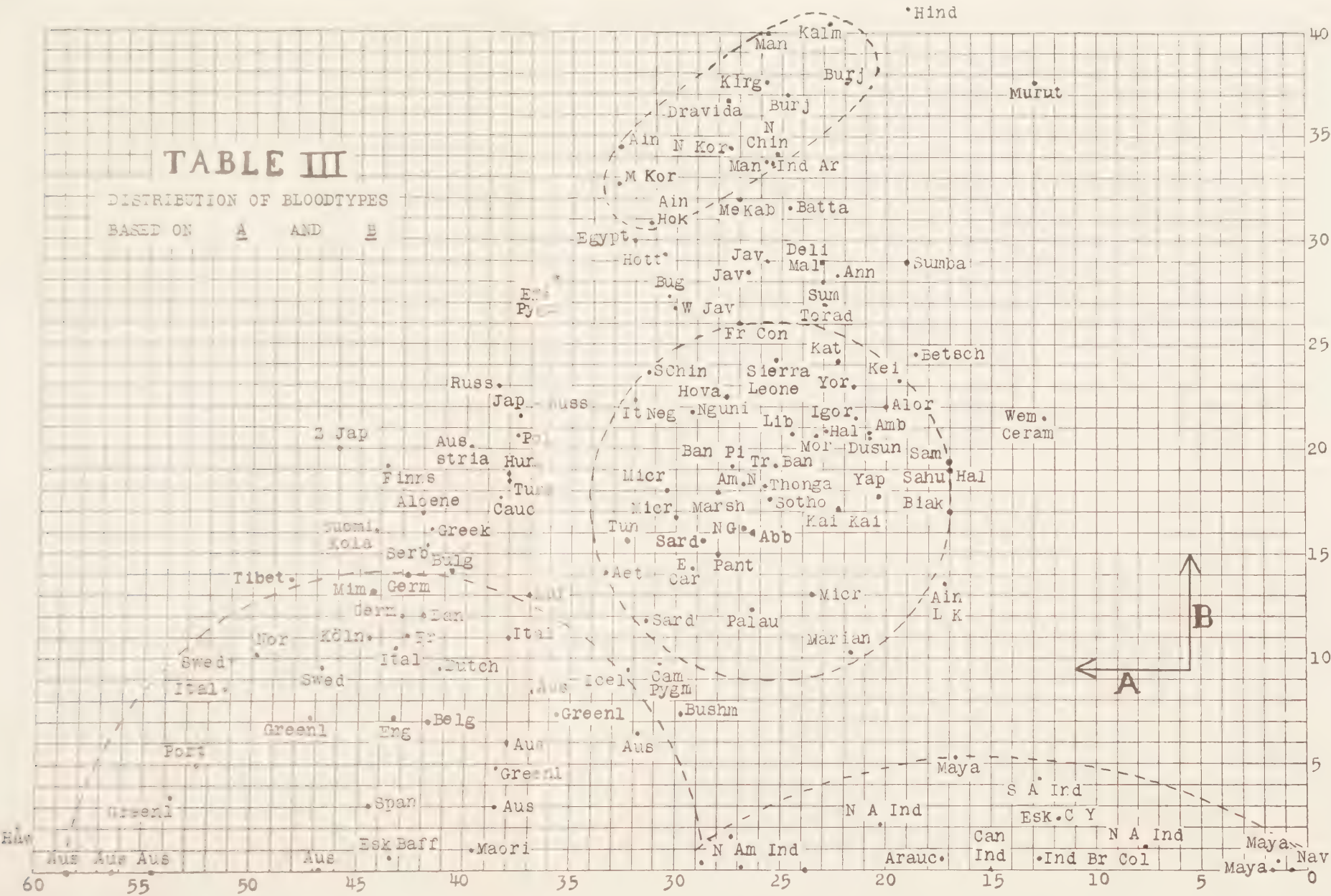
We may briefly discuss the question whether the frequent association of 73—75 and 78—80 index peaks in one group or in closely related groups may be correlated with stature differences or with other factors, e.g. sex.

It is well known that the average index in dolicho-mesocephalic groups usually is about one point higher with the females than with the males. That this also may be expressed in the peaks appears from the Australian cephalic curves added to our preceding paper, the highest male peaks (Table I fig. 10) being at 70 and 73, the highest female peaks (Table I fig. 13) at 71 and 74. The same appears with the Nesiots whose chief male peak is at 75, the female at 76 (*ibidem*, Table I figs. 1 A and 12).

The sexual difference in curves, however, may be also such that, as with the Ainou (Table II of this paper fig. 6), the female indices partly fall in the higher, i.e. in the meso-subbrachycephalic group, while the male indices fall in the dolichocephalic one. The same, though to a much smaller extent, is observed with our Australian females, which have small additional 78—80 peaks, failing with the males.

However, since females usually have a smaller stature, the differences referred to might be also correlated with stature alone. The correlation of skull index and stature, so well known in animals since KLATT's work on this subject, has been stated also in man, especially by PITTARD and DONICI and by KLEIWEIG DE ZWAAN, who found that in closely related individuals of different stature the group with the smallest stature had a higher average index. This might be brought forth in order to explain the greater frequency of the higher indices with the African and New-Guinea Pygmies, where the 77(8)—80 peaks are dominating also in the males. With the Pesechem and Baining the brachycephalisation goes still further, as it also does with the Andamanese and Philippine Negritos.





Most of the racial or group names on this map speak for themselves. Of some abbreviations the explanation is as follows:

Abb = Abyssinians; Aet = Aeta of the Philippines; Ain Hok = Ainu from Hokkaida; Ain L.K. = Ainu from the Liu Kiu islands; Aloene = Aloene tribe from Ceram (Bijlmer); Am N = American Negroes; Amb = Ambonese (Bijlmer); Ann = Annamites; Aus = Australian groups; Ban Pi = Bantu typed by Pirie; Ban Tr = Bantu from the Transvaal (Pijper); Betsch = Betschuana land; Bug = Bughis (Celebes); Cam-Pygm = Cameroon Pygmies (Julien); Esk Baff = Eskimoes from Baffins land; Esk C.Y. = Eskimoes from Cape York (West Greenland); Fr = French; Fr Con = French Congo; Greenl = Greenland Eskimoes; Hal = Halmaheira; Haw = Hawaiians; Igor = Igorotes; Ind Ar = Indo-Aryans; It Neg = Ituri Negroes (Julien); Kat = Katanga Negroes; Lib = Liberian Negroes (Julien); Kei = Kei islanders; Man = Manchu; M Kor = Middle Koreans; Me Kab = Menang Kabau; Marsh = Marshall islanders; Mim = Mimika Papuans (Bijlmer); Mor = Moroccans; NG = New Guineans; Hova = Hova; Pant = Pantarese (Bijlmer); Sahu Hal = Sahu tribe on Halmaheira (Bijlmer); Sam = Samoans (Stephenson); Sard = Sardinians; Sum = Sumatrans; Torad = Torad; Wem = Wemale tribe from Ceram (Bijlmer); Yor = Yoruba Negroes.

The Nguni, Thunga and Sotho, typed by Elsdon-Dew, are Bantu tribes, the Murut and Dusun Borneo Dayaks, typed by RIDE. For more data see WELLISCH' and STEFFAN's Handbuch der Blutgruppenkunde. Lehmann, München, 1932. —

Even the prevailing dolichocephalic dwarfish Veddah from Ceylon (average male stature 153 cm.) differ from their closest relatives, the Australian aboriginals with whom the main body of their male cranial indices (textfig. 1) corresponds, by having an additional 75 and 78 cranial peak, a phenomenon equally observed on comparing the cephalic curves of both groups¹⁾, registered in textfigure 2. However, the fact that the majority of the Veddah are dolichocephalic, and — on the other hand — the frequent occurrence of 77(8)—80 cephalic (75(6)—78 cranial) peaks in much taller tribes in Africa as well as in Oceania, shows that the meso-sub-brachycephalic variation, though favoured by small stature, is by no means always correlated with it. Apparently also other factors act a part in the increase of the index, among which probably also the increase of the brain, since there is evidence to show that the 78—80 index usually is combined with a greater skull capacity than the lower indices (BOLK, DIJKSTRA, PICKERING²⁾).

Another point is the relation between the so frequently occurring central Eurasian 79—81 cephalic peak curve and the 78—80 peak cephalic curve. Although the difference between these peaks is one point only, the frequent occurrence of the 79—81 peaks in curves of more central Eurasian peoples and their very rare occurrence in the curves of African, Oceanian and Atlantic-Nordic peoples suggests that, apart from other anthropological differences there may be special factors producing the 79—81 index peak curve.

In this connection I may again refer to the fact that, wherever 78—80 peaks are found on the Eurasian continent, either with Mongoloid or with non-Mongoloid groups, among these groups frequently a good number of the more primitive 73—75(6) index type is found. On the contrary the Eurasian 79—81 index groups, published in another paper³⁾, very rarely show a combination with the more primitive 73—75(6) peaks.

The less primitive character of the 79—81 index curve also appears from the fact that the 79—81 curves often show additional brachycephalic, viz. 83 and 86 peaks.

That this may lead to prevailing 83—86 index peaks, which also may revert again in the 79—81 peak type, was shown in preceding papers⁴⁾ on the ground of the data published by BOAS, GUTHE and HIRSCH. In this connection also KLEIN's researches on the developmental changes of this index are important⁵⁾.

SUMMARY⁶⁾.

Frequency curves of cephalic and cranial indices of Nesiots and Melaneseans show that their prevailing index peaks correspond with those of the African Melanoderms, viz. the 73—75 and 77(8)—80 cephalic or the 71—73 and 75(6)—78 cranial peaks. The middle circle in Table III shows the same for the majority of their blood groups.

With both the African and Oceanian Melanoderms Pygmy varieties occur with 77(8)—80 peaks, but with both also taller people with

¹⁾ I am greatly indebted to prof. E. VON EICKSTEDT for giving me the individual data of his important Veddah measurements.

²⁾ Amer. Journ. of physical Anthropology, Vol. 15, 1930.

³⁾ Proc. Royal Acad. Amsterdam, 37, 602 (1934).

⁴⁾ Proc. Royal Acad. Amsterdam, 38, 686 (1935) and Ibidem p. 989.

⁵⁾ Proc. Royal Acad. Amsterdam, 38, 1021 (1935).

⁶⁾ Of this and our preceding article (Volume 39, p. 1156).

prevailing 77(8)—80 peaks occur. With the Pesechem and Baining Pygmies a further brachycephalisation takes place.

While the wide spread of the 75 cephalic (73 cranial) peak groups shows their great viability, the frequent combination of the 75 with the 77(8)—80 peak type indicates their inherent progressive tendency. On the other hand, the far more localized "Australoid" 73 cephalic (71 cranial) and its usual combination with much lower index peaks indicates a more or less asthenic, regressive character of these groups.

Indo-Melanesoid index curves are also found in the Polynesian islands (with the more ancient population chiefly) and furthermore in Southern California, Ecuador, Peru, Brazil, with the Patagonians, Fuegians and several North American Indian groups, thus showing that a primitive 75—77(8)—80 index people — now differentiated in various sub-races — has extended over the whole earth in its greatest intertropical width.

On the Asiatic continent analogous frequency curves are found with the Melanoderm Dravidians (an Australoid curve with the Veddah) but also with the non-prognathous, depigmented and further differentiated Indo-Aryans, Makhiani, Persians, Kurds and Ainou and with paleo-mongoloid South Eastern Asiatics such as the Shan, Palaung, Pamirese, and Tibetans, the paleo-Siberian Ob-Ostyaks and Yakughirs.

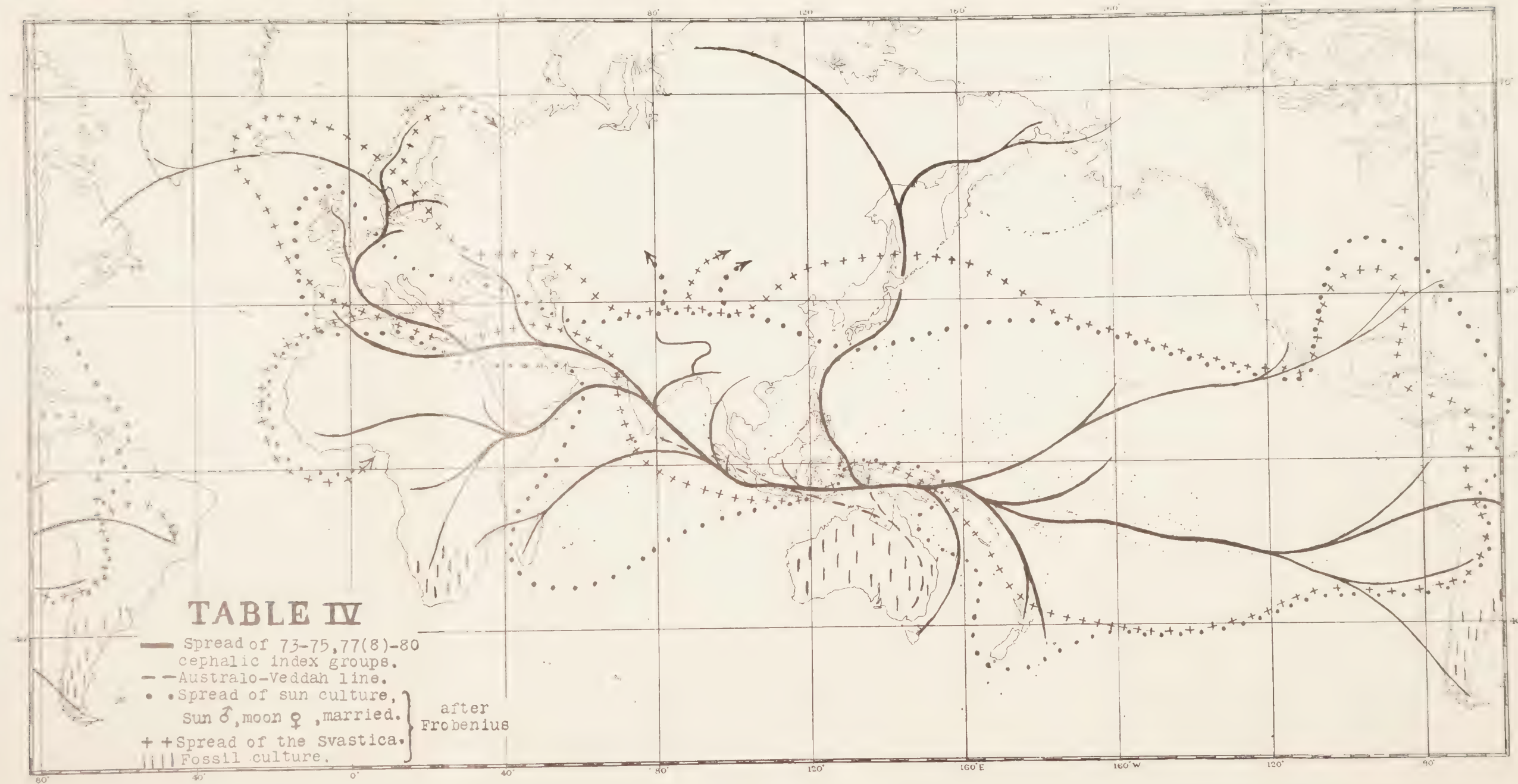
The Eskimoes also show primitive index curves. The relationship between the Western and Eastern groups is such that with the Greenland Eskimoes the more primitive dolichocephalic peak prevails, with the Alaska Eskimoes its more progressive mutation (78; cf. Table II, fig. 9). This relationship is still more evident in the cranial curves (Table I, fig. 14). — The resemblance of the Alaska curves and the paleo-Siberian and Ainou curves suggests East Asiatic affinities. The blood type of the Greenland Eskimoes (Table III) closely approaching the Mediterraneo-Atlantic blood type raises the question if their European relationship (RUGGLES GATES) may not be of a very ancient date, as suggested by the Chancelade skull.

A comparison of the paleolithic, neolithic and recent Mediterraneo-Atlantic groups of Western Europe shows that the 76—78 cranial (= 78—80 cephalic) group increased in the course of time and especially in northern direction at the expense of the 71—73 cranial (73—75 cephalic) group. This as well as the occasional occurrence of 73—75 peaks with the 77(8)—80 Nordic peaks strongly suggests that the meso-sub-brachycephalic group may be partly a mutation of the 73—75 cephalic group.

The anthropological relationship established between the Pacific, southern Asiatic and Mediterraneo-Atlantic (Nordic) groups agrees with FROBENIUS¹⁾ and KOHLBRUGGE's ethnographic conclusions (Table IV). Our results strongly plead for a monophyletic origin of humanity²⁾.

¹⁾ FROBENIUS, *Vom Kulturreich des Festlandes*, München-Nymphenburg, 1923.

²⁾ Space does not allow to quote the extensive literature consulted for the data registered in our curves. The authors, however, are mentioned on the figures.



Physics. — *Research on thin layers of tin and other metals. III. The interaction between metals and lubricating oils.* By P. J. HARINGHUIZEN and D. A. WAS. (Communicated by Prof. L. S. ORNSTEIN).

(Communicated at the meeting of December 19, 1936).

Summary.

The corrosion of copper, tin and lead, and the influence of these metals upon the deterioration of lubricating oils have been studied. The viscosity, the surface tension and the acidity are not influenced. It appears that copper stimulates the sludge formation, while tin and lead act as anti-oxidants. The amount of sludge depends on the percentage of aromatic compounds in the oil.

The corrosion has been investigated by an optical method. Copper is strongly attacked; tin and lead are protected by a film of reaction products. The corrosive properties of the oil are influenced by storing.

Introduction.

In preceding papers we have communicated investigations on the corrosion of metals by technical insulating oils ¹⁾ and on the influence of these metals upon the deterioration of these oils ²⁾. It seemed interesting to extend this work on lubricants.

We used four well-known commercial motor-oils, hereafter designated as oils *L*, *M*, *N* and *O*. They were guaranteed as having the respective S.A.E. numbers 50, 30, 30 and 20. We have investigated the deterioration of the oils and their corrosive effect on metals, and have also tried to ascertain their chemical composition.

§ 1. *The deterioration of the oils.*

The deterioration was caused by heating 50-cc samples in glass basins at 96° C. for 1350 hours in an electrical furnace. This choice of the temperature was such, that it is in the neighbourhood of that which will occur in practice. At this temperature no cracking of the oil takes place. For comparison of the action of tin, copper and lead, thin layers of these metals were placed in the oils. The layers (area 5 cm²) were obtained on glass plates by means of high vacuum evaporation.

¹⁾ P. J. HARINGHUIZEN and D. A. WAS, Proc. Royal Acad. Amsterdam, **39**, 201 (1936). Tech. Publ. of the Intern. Tin Research and Development Council, Series A N^o. 35.

²⁾ P. J. HARINGHUIZEN and D. A. WAS, Proc. Royal Acad. Amsterdam, **38**, 1002 (1935). Techn. Publ. of the Intern. Tin Research and Development Council, Series A N^o. 29.

The effectivity of a lubricant depends on the viscosity, the surface tension and the amount of sludge. Therefore we investigated the variation of these properties for the oils after deterioration.

The viscosities of the original and of the deteriorated oils were measured with the VOGEL-OSSAG-standard viscosimeter at the temperatures 20, 50 and 70° C. It appeared that the viscosity is increased by the deterioration, but that the action of the metals was not specific and the differences between the blank experiments and those samples which were deteriorated with metal was not great. It is possible that the increase is not only caused by oxidation, but that also the evaporation of the most volatile parts of the oils has an influence.

During oxidation acids may be formed. However, neither in the original nor in the deteriorated oils were free acids found. In order to determine the esterified acids, we measured the saponification value, according to the method given by the V.D.E. The figures obtained are plotted in table I.

TABLE I.
Saponification value.

Oil	Original oil	Deteriorated with			Blank exp.
		copper	tin	lead	
<i>L</i>	0.08	0.10	0.12	0.15	0.11
<i>M</i>	0.05	0.54	0.47	0.61	0.41
<i>N</i>	0.21	1.21	1.24	1.22	1.22
<i>O</i>	0.04	1.70	1.49	1.68	1.40

These figures show that the influence of the metals on the increase of saponifiable substance is very small. Oil *O* shows the greatest increase, followed by oil *N*, oil *M* and oil *L*, respectively.

The fact that the saponification value is so small indicates the absence of fatty oils, which are sometimes added to lubricants.

The surface tension was measured by means of the method that depends on the force necessary to remove a ring from the surface; this force being measured by a torsion balance.

It appears that the different oils have about the same surface tension (29 to 30 dynes/cm), which is exactly the same after deterioration.

The quantity of sludge greatly influences lubrication. Therefore we measured the sludge formed by filtering the oil through a B_2 -crucible, the sludge being washed out with gasoline and dried at 90° C.

The quantities of sludge (expressed in mgrs) formed in 50 cc of oil are given in Table II.

Considering the results of the blank experiments, it is remarkable that there is such a large difference between the oils. Oil *L* does not form any

TABLE II.
Sludge in millidrams per 50 cc of oil.

Oil	Deteriorated with			Blank exp.
	copper	tin	lead	
<i>L</i>	0	0	0	0
<i>M</i>	43.5	0.3	1.3	14.5
<i>N</i>	73.9	2.2	2.4	15.0
<i>O</i>	749	57	59	747

sludge within the period of 1350 hours of deterioration; on the other hand, oil *O* is strongly oxidized. The values for oils *M* and *N* are of the same order.

It is also remarkable that in this case the action of the metals is so extremely different; while copper stimulates the sludge formation, tin and lead on the contrary show a strong anti-oxidizing action.

In this connection we may point to the result of MARDLES¹⁾ who investigated the catalyzing effect of tin on lubricants at higher temperatures.

The connection of this difference with the character of the oils is most interesting. We have, therefore, computed constants, which depend on the chemical composition of the oil. Thus we have measured the aniline-points, the specific gravities *D* 20/4, the mean molecular weights, the specific refractions (LORENTZ-LORENZ) and the specific dispersion of the oils. Table III gives the results:

TABLE III.

Oil	Visc. Index	Spec. Grav.	Spec. Dispersion	Spec. Refraction	Aniline point	Mean mol. weight
<i>L</i>	82	0.8864	173	0.3256	114.0	599
<i>M</i>	103	0.8782	167	0.3281	112.2	543
<i>N</i>	95	0.8804	174	0.3280	114.5 ⁵	579
<i>O</i>	94	0.8806	172	0.3280	105.1 ⁵	512

VLUGTER, WATERMAN and VAN WESTEN²⁾ described a method which enables the chemical composition to be calculated from the aniline-point, the specific refraction and the mean molecular weight. We can, using their method, dispense with the hydrogenation of the oil.

From the figures of Table III follows the composition given in Table IV.

¹⁾ E. W. J. MARDLES, D. Sc.: Tech. Publ. of the Int. Tin Research and Development Council, Series C No. 2.

²⁾ VLUGTER, WATERMAN and VAN WESTEN, J. Inst. Petr. Techn. 18, 735 (1933).

TABLE IV.

Oil	% aromatic ring	% naphthenic ring	% paraffin
<i>L</i>	7	23	70
<i>M</i>	8	14	78
<i>N</i>	8	13	79
<i>O</i>	11	15	74

A comparison of these figures with those of Table II shows that there is a parallelism between the percentage of aromatic compounds and the sludge formation. This supports the conception that sludge formation is caused by oxidation of aromatic substances. The process, however, is highly influenced by the character of the metal. The fact that the formation of acids is not affected by the metals, shows that they are formed from other compounds.

§ 2. *The corrosion of the metals.*

The corrosion has been investigated by the optical method, described in our preceding publication¹⁾. The principle of the method can be summarized as follows: metal films, obtained by high vacuum evaporation, of a thickness so that they show a measurable transmission for light, were corroded. This causes an increase in light transmission; the relation between the thickness of the layer and this transmission being known experimentally, our measurements give the corrosion as a function of the time. For experimental details we refer to the paper mentioned above.

We have studied the attack of the oils on copper, tin and lead at 96° C. In Fig. 1 is plotted the corrosion of copper as a function of the time. It appears to be relatively violent; contrary to the process with insulating oils, no protective film of reaction products is formed on the surface. The formation of such a layer would cause the curve to run horizontally. The films of metal completely dissolved. To demonstrate this fact more clearly, we also have plotted (dotted line) the curve for a thick film, which we estimate at more than 100 γ per cm². In some cases (in oil *O*) the corrosion was still more violent (viz. 100 γ per cm² in 70 hours).

With tin and lead, on the contrary, the protective film was always formed. Fig. 2 shows curves obtained in oils *L* and *M*. Tin and lead are differently corroded; which metal is most strongly corroded depends on the oil.

In oils *N* and *O* the corrosion is greater and the curves were less repro-

¹⁾ P. J. HARINGHUIZEN and D. A. WAS, Proc. Royal Acad. Amsterdam, **39**, 201 (1936). Tech. Publ. of the Intern. Tin Research and Development Council, Series A N^o. 35.

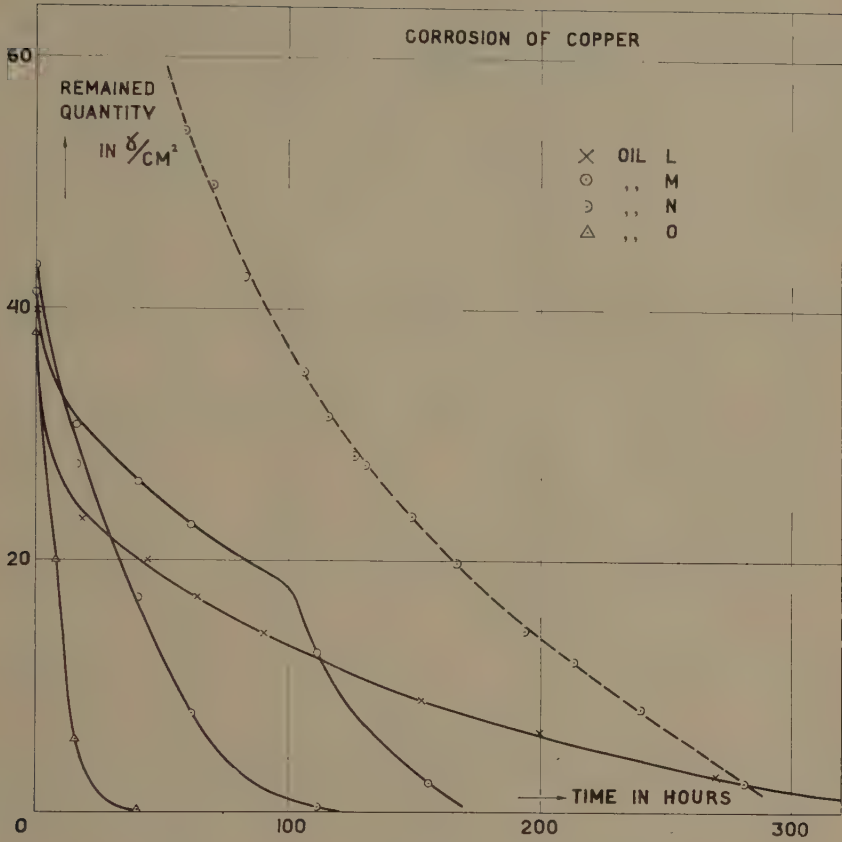


Fig. 1.

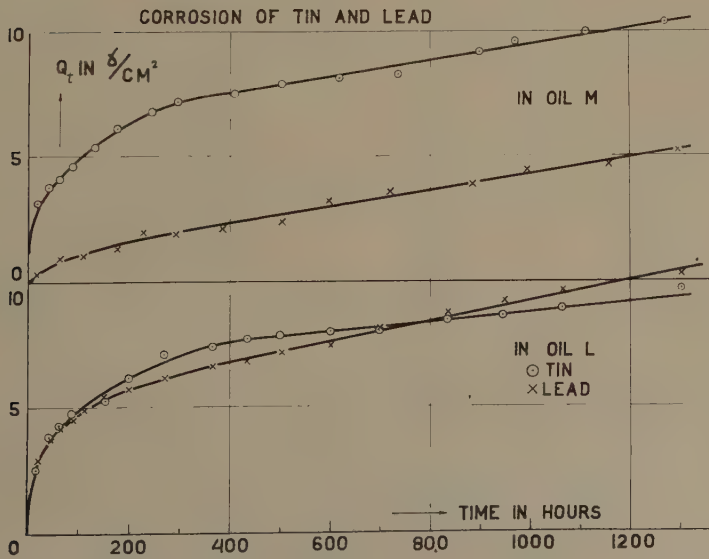


Fig. 2.

ducible. Sometimes the protective film is destroyed, but is always formed again. In these oils tin is somewhat more corroded than lead.

From the shape of the curves and especially from the appearance of the straight line, we can conclude that the corrosion process is the same as in technical insulating oils. The theory developed in the preceding paper can also be applied to these results.

With the aid of the experimental formula $Q_t = \frac{\alpha t}{1 + \beta t} + \eta t$ the constants α , β and η can be determined graphically.

The theoretical considerations giving the following relations:

$$\alpha = \frac{A^2}{A + D/\delta} c_0; \beta = \frac{A + D/\delta}{2} \text{ and } \eta = \frac{A D/\delta}{A + D/\delta} c_0$$

where A is a reaction constant,

D the diffusion constant,

δ the thickness of the protective film and

c_0 the concentration of the corroding agent.

These values can be calculated.

The results derived from the curves of Fig. 2 are given in Table V.

TABLE V.

Metal	Oil	$\alpha \cdot 10^4$	β	$\eta \cdot 10^5$	A	$D/\delta \cdot 10^4$	C_0 in γ mol./cc
<i>Sn</i>	<i>L</i>	11.5	0.018	1.60	0.037	4.95	0.032
<i>Sn</i>	<i>M</i>	14.5	0.026	2.69	0.052	9.6	0.028
<i>Pb</i>	<i>L</i>	11.8	0.045	1.93	0.092	15.0	0.013
<i>Pb</i>	<i>M</i>	0.97	0.016	1.57	0.031	51.0	0.003
<i>Pb</i>	<i>O</i> (1)	2.2	0.013	1.2	0.026	14	0.0085
<i>Pb</i>	<i>O</i> (2)	12.6	0.032	1.7	0.064	8.5	0.020
<i>Pb</i>	<i>O</i> (3)	7.2	0.0087	1.0	0.017	2.4	0.042

We may point out that the values of C_0 are of the same order as those obtained with technical insulating oils.

A remarkable fact is that, if the oils are stored for some months their corrosivity is increased. This is demonstrated by Fig. 3 in which are plotted the curves for lead in oil *O*, started respectively at 24/1, 3/6 and 20/8 1936. With tin a smaller effect appeared.

The curves of Figures 1 and 2 refer to measurements with fresh oils.

The values of A , D/δ and C_0 computed from the curves of Fig. 3 are

also plotted in Table V (indicated by 1, 2, 3). It appears that the value of C_0 increases with storage.

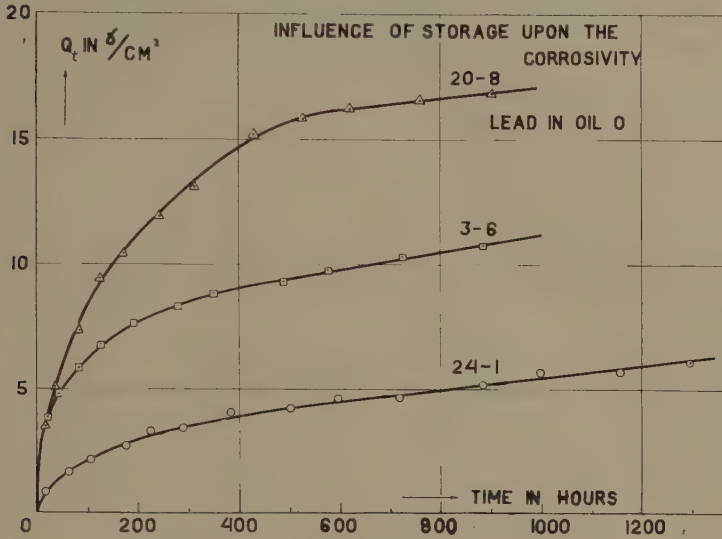


Fig. 3.

Oil *L* is sold in sealed cans. It was observed that oil stored in opened cans is much more corrosive. Even breakdowns of the protective films occur. Also oil out of a can that has been opened and sealed again and then stored for a month, shows this effect. The results are given in Fig. 4.

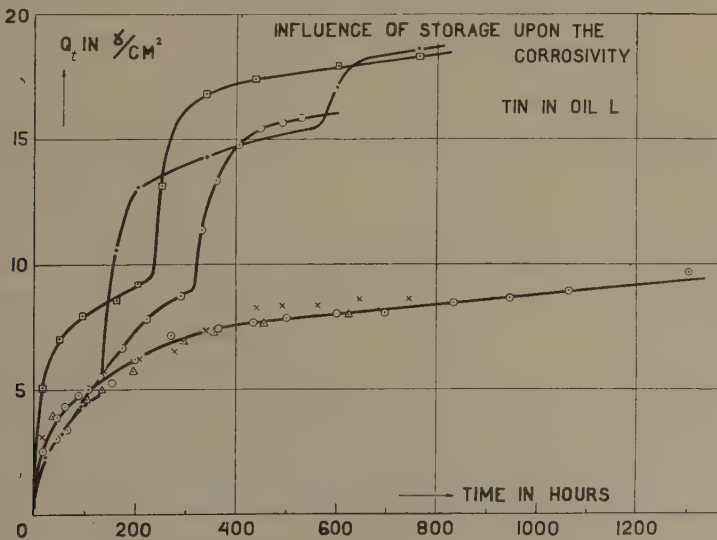


Fig. 4.

- △ × of three cans, not opened before,
 ○ after 4 months storage in opened can,
 □ " 5 1/2 " " " " "
 ● " 1 month " " can opened and sealed again.

Apparently this effect is connected with the absorption of air during the storage of the oils. This, however, requires a further investigation.

To summarise the results of the comparison of the metals: Copper is very strongly attacked; the corrosion of tin and lead is much smaller — due to the formation of protective films — and is of about the same order for both metals.

Acknowledgment.

The authors wish to thank the International Tin Research and Development Council for permission to publish this paper and for the grant which enabled this work to be carried out.

For his stimulating interest we express our sincere thanks to Prof. Dr. L. S. ORNSTEIN, who has kindly directed the work.

We also are indebted to Ing. D. J. W. KREULEN for his valuable advice on the determination of the chemical composition of the oils.

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Mathematics. — *Ueber die Gitterpunktzahl auf und in der Umgebung gewisser Kurven*¹⁾. Von D. SCHEPEL Kzn. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of December 19, 1936).

Das Problem eine obere Schranke für die Gitterpunktzahl auf einer Kurve oder in ihrer Umgebung zu bestimmen, kommt in der Zahlentheorie vielfach vor. In einigen Fällen wird ein sehr genaues Ergebnis erreicht. Bekanntlich ist zum Beispiel die Anzahl der Gitterpunkte auf jeder Kreis-peripherie mit Radius $R > 2$ für jede positive Zahl ε höchstens von der Grössenordnung R^ε . Ebenso ist die Gitterpunktzahl auf der Hyperbel $uv = x$, wo $x > 2$ ist, für jedes positive ε höchstens von der Grössenordnung x^ε .

Ein so scharfes Resultat ist nur für sehr spezielle Kurven erreicht worden.

Mir ist jedoch ein Satz bekannt, der in sehr allgemeinen Fällen eine nicht triviale obere Schranke liefert für die Anzahl der Gitterpunkte auf einer Kurve oder in ihrer Umgebung. Der betreffende Satz ist der Hauptsatz in der Dissertation von Herrn J. G. VAN DER CORPUT²⁾. Dieser Satz lautet folgendermassen:

¹⁾ Diese Abhandlung ist zugleich Einleitung meiner Groninger Dissertation (1937).

²⁾ J. G. VAN DER CORPUT, Over roosterpunten in het platte vlak. Groningen 1919. Diss. Leiden.

Es sei $a < b$; $a - \frac{1}{2}$, $b - \frac{1}{2}$ und $q - \frac{1}{2}$ seien ganz. Die Funktion $f(u)$ sei im Intervall $a \leq u \leq b$ mindestens zweimal differenzierbar und $f(a) > q + 1$. Ueberdies gebe es eine Zahl $r > 1$, derart dass $f'(u) > \frac{1}{\sqrt[r]{r}}$ und $f''(u) > \frac{1}{r}$ für jedes u im Intervall $a \leq u \leq b$ ist.

Es bezeichne \mathfrak{G} das Gebiet

$$a \leq u \leq b, \quad q \leq v \leq f(u),$$

$I(\mathfrak{G})$ seinen Flächeninhalt

$$I(\mathfrak{G}) = \int_a^b (f(u) - q) du,$$

$A(\mathfrak{G})$ die Anzahl der ihm angehörigen Gitterpunkte

$$A(\mathfrak{G}) = \sum_{h=a+\frac{1}{2}}^{b-\frac{1}{2}} ([f(h)] - [q]) \quad {}^3).$$

Dann gilt

$$|A(\mathfrak{G}) - I(\mathfrak{G})| < cr^{\frac{2}{r}} f'(b),$$

wo c eine absolute Konstante bezeichnet.

Zunächst folgt hieraus, dass die Anzahl der Gitterpunkte auf der Kurve

$$a \leq u \leq b, \quad v = f(u) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

höchstens gleich $2cr^{\frac{2}{r}} f'(b)$ ist; denn wird die Kurve parallel nach oben verschoben, so ändert sich $I(\mathfrak{G})$ stetig, sodass die Sprünge höchstens gleich $2cr^{\frac{2}{r}} f'(b)$ sind.

Zugleicherzeit kann man mit dem VAN DER CORPUTSchen Satze eine obere Schranke finden für die Anzahl der Gitterpunkte, die in der Umgebung der Kurve (1) liegen. Betrachtet man nämlich den Streifen ⁴⁾

$$a \leq u \leq b, \quad -\delta \leq v - f(u) \leq \delta,$$

wo δ eine beliebige feste positive Zahl bezeichnet, so erhält man mittels

³⁾ Für reelles a bezeichnet $[a]$ die grösste ganze Zahl $\leq a$. Der VAN DER CORPUTSche Satz, wie er hier formuliert ist, folgt z.B. sofort aus der von Herrn LANDAU angegebenen Fassung. Vergl. E. LANDAU, Vorlesungen über Zahlentheorie, 1927 (S. HIRZEL), Band 2, S. 192 und 279—302.

⁴⁾ Ist $a < b$, sind $f(u)$ und $\sigma(u)$ im Intervall $a \leq u \leq b$ definiert und ist dort $\sigma(u)$ eine positive Funktion von u , so verstehe ich unter dem Streifen

$$a \leq u \leq b, \quad -\delta(u) \leq v - f(u) \leq \delta(u) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

die Menge der Punkte (u, v) , wofür (2) gilt.

zweifacher Anwendung des VAN DER CORPUTSchen Satzes, dass die Anzahl der Gitterpunkte in diesem Streifen kleiner ist als

$$2cr^{2/3}f'(b) + 2(b-a)\delta.$$

Dieser Satz hat zwei Nachteile. Erstens fordert er einen, wenigstens bis heute, komplizierten Beweis ⁵⁾. Weiter ist der Satz nur anzuwenden, wenn die Funktion eine zweite Ableitung besitzt, die gewissen Bedingungen genügt.

Das Ziel meiner Dissertation ist in elementarer Weise einige Sätze herzuleiten, die diese Nachteile nicht besitzen und dennoch für die Anzahl der Gitterpunkte auf und in der Umgebung von Kurve (1) eine brauchbare obere Schranke geben.

Meine Dissertation habe ich in sechs Kapitel zerlegt. Die Kapitel I, V und VI enthalten allgemeine Sätze, während die drei übrigen Anwendungen der in Kapitel I hergeleiteten Sätze geben. Die im letzten Kapitel entwickelte Theorie stützt sich auf die Theorie der FAREY-brüche, aber diese Theorie kommt in den fünf vorangehenden Kapiteln nicht vor.

Um den Gedankenkreis der Kapitel I, II, III und IV anzugeben, nehme ich hier in der Einleitung Satz 1 auf, den ich in Kapitel I beweisen werde.

Satz 1. Sei $\delta \geq 0$ und $< \frac{1}{2}$, $\alpha < \beta$, k ganz ≥ 2 ; sei die Funktion $f(u)$ im Intervall $\alpha \leq u \leq \beta$ definiert und k -mal differentiierbar; seien weiterhin die von u unabhängigen positiven Zahlen r und R so gewählt, dass im Intervall $\alpha \leq u \leq \beta$

$$r \leq |f^{(k)}(u)| \leq R$$

ist; dann ist die Anzahl der Gitterpunkte (u, v) im Streifen

$$\alpha \leq u \leq \beta, \quad -\delta \leq v - f(u) \leq \delta \quad (3)$$

höchstens gleich

$$k + k(\beta - \alpha) \text{Max} \left\{ R^{\frac{2}{k(k+1)}}, \left(\frac{(k+1)\delta}{r} \right)^{\frac{2}{k(k-1)}} \right\} \quad 6).$$

Dieser Satz, der, wie gesagt, in einfacher Weise bewiesen wird, hat den grossen Vorteil, dass darin für k eine beliebige ganze Zahl ≥ 2 genommen werden kann.

Der Spezialfall $k=2$ stimmt etwa überein mit dem Ergebnis, das man erhält, wenn man den VAN DER CORPUTSchen Satz auf die Lehre der Gitterpunkte auf oder in der Umgebung einer Kurve anwendet.

⁵⁾ Man vergleiche z.B. den LANDAUSchen Beweis.

⁶⁾ Unter $\text{Max}(a, b)$, Maximum von a und b , wird die grössere der Zahlen a und b oder, falls $a = b$ ist, ihr gemeinsamer Wert verstanden.

Zur Erläuterung der Kapitel I, II, III und IV skizziere ich hier kurz den Beweis des vorstehenden Satzes im Spezialfall $k=2$:

Enthält der genannte Streifen drei Gitterpunkte (p_0, q_0) , (p_1, q_1) und (p_2, q_2) , so ist, wie sich leicht herausstellt, das Verhältnis

$$\begin{array}{c|ccc} & 1 & 1 & 1 \\ & p_0 & p_1 & p_2 \\ & q_0 & q_1 & q_2 \\ \hline 1 & 1 & 1 & 1 \\ p_0 & p_1 & p_2 \\ \frac{1}{2} p_0 (p_0 - 1) & \frac{1}{2} p_1 (p_1 - 1) & \frac{1}{2} p_2 (p_2 - 1) \end{array} \quad \cdot \cdot \cdot \cdot \quad (4)$$

annähernd gleich $f''(\xi)$ bei geeignet gewähltem ξ und je schmaler der Streifen um so schärfer ist die Approximation.

Im Spezialfall $k=2$ von Satz 1 wird $f''(u)$ ungleich Null vorausgesetzt. Bei genügend klein gewählter Streifenbreite verschwindet also das in (4) genannte Verhältnis nicht. Der darin vorkommende Zähler ist deshalb nicht gleich Null, also sein Absolutwert ist ≥ 1 , woraus hervorgeht, dass der Nenner mindestens dieselbe Grössenordnung als $\frac{1}{|f''(\xi)|}$ hat, also gross ist, falls $f''(u)$ klein angenommen wird.

Hieraus folgt, dass die drei Zahlen p_0 , p_1 , und p_2 nicht dicht bei einander liegen können. Je drei dem Streifen angehörigen Gitterpunkte haben also die Eigenschaft, dass die zwei äusseren weit von einander entfernt sind, sodass es ausgeschlossen ist, dass der Streifen viele Gitterpunkte enthält.

Mit dieser, in Kapitel I näher ausgearbeiteten Methode finde ich für die dem Streifen (3) angehörigen Gitterpunktzahl eine obere Schranke, nicht nur für den Spezialfall $k=2$, sondern für beliebiges ganzes $k \geq 2$.

Bei der Anwendung von Satz 1 wird oft die Schwierigkeit auftreten, dass für grosses $\beta - \alpha$ die Zahl R viel grösser als r gewählt werden muss. Um dennoch ein scharfes Ergebnis zu erhalten, ist es notwendig den betrachteten Streifen in Teilstreifen zu verteilen. Weil diese Verteilung die Beweisführung manchmal undurchsichtig macht, wird in Kapitel I noch ein zweiter Satz hergeleitet, wobei man diese Verteilung nicht braucht. Gerade dieser zweite Satz wird in den Kapiteln II, III und IV angewendet.

In Kapitel II bestimme ich eine obere Schranke für die Anzahl der Gitterpunkte (u, v) auf und in der Umgebung der Kurve

$$(mu + u_0)^f (nv + v_0)^h = x, \quad mu + u_0 > 0, \quad nv + v_0 > 0, \quad \cdot \cdot \cdot \quad (5)$$

worin f , h , m und n positive, und u_0 und v_0 beliebig feste Zahlen sind.

Z.B. hat Satz 9 in diesem Kapitel, wie aus Satz 10 hervorgeht, u.a. das folgende Korollar:

Satz 2. Sind u_0 und v_0 beliebige feste, m , n , f und h beliebige feste positive Zahlen und ist k eine ganze Zahl ≥ 3 , derart dass

$$\frac{(k-1)(k-2)}{2} \leq \frac{f}{h} < \frac{k(k-1)}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

gilt, so ist die Anzahl der Gitterpunkte (u, v) im Streifen

$$-X \leq (mu + u_0)^f (nv + v_0)^h \leq X, \quad mu + u_0 > 0, nv + v_0 > 0,$$

wobei

$$X = x \operatorname{Min} \left(x^{-\frac{1}{h}}, x^{-\frac{2k(k+1)}{2kh + (k+3)f}} \right)$$

ist ⁷⁾, gleich

$$O \left(x^{\frac{k+1}{2kh + (k+3)f}} \right).$$

Wird die Bedingung (6) durch

$$\frac{k(k-1)}{2} < \frac{f}{h} < \frac{k(k+1)}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

ersetzt, wobei k ganz ≥ 2 ist, so ist, wie Satz 11 zeigt, die Anzahl der der Kurve (5) angehörigen Gitterpunkte (u, v) gleich

$$O \left(x^{\frac{2k}{(k+1)(2f+kh)}} \right).$$

Aus dem Satze in § 88 der Dissertation von Herrn J. G. VAN DER CORPUT geht hervor: die erwähnte Gitterpunktzahl auf der Kurve (5) ist gleich

$$O \left(x^{\frac{1}{3f} \log x} \right), \quad \text{falls } f = h$$

und

$$O \left(x^{\frac{1}{2f+h}} \right) + O \left(x^{\frac{1}{f+2h}} \right), \quad \text{falls } f \neq h.$$

Wende ich Satz 2 mit $k=3$ an, so erhalte ich u.a. dass die Anzahl der Gitterpunkte auf der betrachteten Kurve (5) für $f=h$ gleich $O \left(x^{\frac{1}{3f}} \right)$ ist; dieses Ergebnis ist schärfer als das vorangehende VAN DER CORPUTSche Resultat.

Ausserdem ist für $f > h$ (da in diesem Falle

$$\frac{k+1}{2kh + (k+3)f} < \frac{1}{f+2h} \quad \text{und} \quad \frac{2k}{(k+1)(2f+kh)} < \frac{1}{f+2h}$$

⁷⁾ Unter $\operatorname{Min} (a, b)$, Minimum von a und b , verstehe ich die kleinere der Zahlen a und b oder, falls $a = b$ ist, ihren gemeinsamen Wert.

Wie Herr J. F. KOKSMA ¹⁰⁾ im „Zentralblatt“ erwähnt hat, kann man die Ungleichung für $A(a)$ verschärfen. Herr KOKSMA hat nämlich bewiesen:

Wenn $A(a)$ die Anzahl der Gitterpunkte (x, y) ($x > 1, y > 1$) auf der PILLAISchen Kurve (9) bezeichnet, so gilt für jedes positive δ und für jedes $a > a_0(\delta)$, worin $a_0(\delta)$ eine geeignet gewählte nur von δ abhängige Zahl ist, die Ungleichung

$$A(a) \leq (2 + \delta) \frac{\log a}{(\log \log a)^{9/2}}.$$

Dieses Ergebnis hat er jedoch nicht veröffentlicht ¹¹⁾, weil er aufmerksam gemacht wurde auf die Tatsache, dass der VAN DER CORPUTsche Satz ein noch schärferes Resultat ergibt, nämlich dass die Anzahl der Gitterpunkte (x, y) ($x > 1, y > 1$) auf der PILLAISchen Kurve (9) gleich

$$O\left(\frac{\log^{9/2} a}{\log \log a}\right)$$

ist. Dasselbe Ergebnis wird in dieser Dissertation mit Hilfe des Satzes 6 von Kapitel I, also in elementarer Weise, hergeleitet. Ausserdem bestimme ich in Kapitel IV eine obere Schranke für die Gitterpunktzahl in der Umgebung der PILLAISchen Kurve.

Die Sätze des Kapitells I haben den Nachteil, dass sie nur für sehr schmale Streifen mit Erfolg anwendbar sind. Deswegen habe ich in den letzten zwei Kapiteln Sätze hergeleitet, die für verhältnismässig breite Streifen brauchbar sind. Die betreffende Untersuchung hat in Bezug auf die Resultate, nicht in Bezug auf die Beweismethode grosse Ähnlichkeit mit der, welche Herr SKOLEM ¹²⁾ in 1926 veröffentlicht hat. Diese SKOLEMsche Untersuchung besteht hauptsächlich aus drei Teilen:

Im ersten Teil tritt eine Funktion $f(x)$ auf, deren k te Differenzfunktion bei geeignet gewähltem k gegen eine irrationale Konstante strebt; im zweiten Teil konvergiert diese k te Differenzfunktion gegen Null und im dritten Teil treten nur Funktionen auf, die so schnell zunehmen, dass keine einzige ihrer Differenzfunktionen beschränkt ist.

Das Verfahren meiner Dissertation gibt nicht die Möglichkeit auch nur eine Frage dieses dritten Teiles zu behandeln.

Andererseits kommen die Ergebnisse des ersten und zweiten Teiles der SKOLEMschen Arbeit alle in den Kapiteln V und VI vor und erhalten sogar eine bedeutende Ergänzung.

Während Herr SKOLEM bei seinen Problemen die Differenzfunktion einführt, ziehe ich es vor Derivierten zu benutzen, weil diese in der Praxis

¹⁰⁾ Zentralblatt für Math. und ihre Grenzgebiete 5, 1933, S. 53.

¹¹⁾ Die nicht publizierte Abhandlung ist mir freundlichst zur Verfügung gestellt worden.

¹²⁾ TH. SKOLEM, Ganzzahlige Lösungen, Math. Ann. 95, 1926, S. 2—68.

bequemer zu verwenden sind. Dabei werde bemerkt, dass man in den betreffenden Sätzen in meiner Dissertation die Derivierten durch Differenzfunktionen ersetzen darf.

Herr SKOLEM führt zwei neue Begriffe ein und zwar folgendermassen:

Definition 1. Sind μ und ν beliebige positive Zahlen mit $\mu \leq \nu$ und ist $A(\mu, \nu)$ die Anzahl ganzer Zahlen einer aus ganzen Zahlen bestehenden Menge M im geschlossenen Intervall (μ, ν) , so heisse $\frac{A(\mu, \nu)}{\nu - \mu + 1}$ die Dichte der Menge M im Intervall (μ, ν) .

Ist $\lim_{\nu \rightarrow \infty} \frac{A(1, \nu)}{\nu} = g$, so nennen wir g die durchschnittliche Dichte oder kurz die Dichte von M .

Definition 2. Sind $f(u)$ und $\delta(u)$ für $u \geq 1$ definiert und ist $\delta(u)$ eine positive, für $u \rightarrow \infty$ gegen Null strebende Funktion von u , so heisse die Menge der Punkte (u, v) mit

$$-\delta(u) \leq v - f(u) \leq \delta(u)$$

ein der Funktion $\delta(u)$ angehöriger asymptotischer Streifen oder eine der Funktion $\delta(u)$ angehörige asymptotische Umgebung der Kurve $v = f(u)$.

Ersetzt man in Satz 2 von Herrn SKOLEM die k te Differenzfunktion durch die k te Ableitung, so erhält man den folgenden Satz:

Satz 3. Ist k eine natürliche Zahl, $f(u)$ für $u \geq 1$ mindestens k -mal differenzierbar und strebt $f^{(k)}(u)$ für $u \geq 1$ bei unbeschränkt anwachsendem u gegen eine Irrationalzahl C , so hat die Menge der Gitterpunktabszissen in jeder asymptotischen Umgebung der Kurve $v = f(u)$ die Dichte Null.

Dieser Satz wird in Kapitel V hergeleitet. In diesem Kapitel wird aber noch mehr bewiesen. Während Herr SKOLEM nur zeigt, dass

$\lim_{\nu \rightarrow \infty} \frac{A(1, \nu)}{\nu} = 0$ ist, gebe ich für den Zähler $A(1, \nu)$ eine obere Schranke woraus das SKOLEMSche Ergebnis sofort folgt.

Als Beispiel erwähne ich hier

Satz 4. Sei $0 < \delta < \frac{1}{2}$, k ganz ≥ 2 , $\beta \geq \alpha + 1$; besitzt die irrationale Zahl C eine regelmässige Kettenbruchentwicklung, deren Teilnenner beschränkt sind¹³⁾ und ist $f(u)$ ein Polynom k ten Grades in u mit Anfangsglied $\frac{C u^k}{k!}$, so ist die Zahl der Gitterpunkte (u, v) im Streifen

$$\alpha \leq u \leq \beta, \quad -\delta \leq v - f(u) \leq \delta$$

¹³⁾ Diese Bedingung ist z.B. erfüllt, wenn C eine quadratische Irrationalität ist.

höchstens gleich

$$k + c(\beta - \alpha) \delta^{\frac{2}{k(3k+1)}},$$

worin c nur von k und C abhängt.

Das letzte Kapitel steht mit dem zweiten Teil der SKOLEMSchen Abhandlung in Zusammenhang.

Ersetzt man in Satz 4 von Herrn SKOLEM die Differenzfunktion durch die Derivierte und schlieszt man den Wert $k=1$ aus, so findet man den folgenden Satz:

Satz 5. Ist k eine beliebige ganze Zahl ≥ 2 , ist die Funktion $f(u)$ für $u \geq 1$ mindestens k -mal differentierbar und nimmt $f^{(k)}(u)$ bei unbeschränkt anwachsendem u monoton gegen Null ab, aber so dass $\frac{1}{u f^{(k)}(u)}$ beschränkt ist, so hat die Menge der Gitterpunktabzissen in jeder asymptotischen Umgebung der Kurve $v=f(u)$ die Dichte Null.

Dieser Satz wird nicht nur im letzten Kapitel bewiesen, sondern ich finde ausserdem eine obere Schranke für $A(1, v)$, woraus das SKOLEMSche Resultat wieder unmittelbar folgt.

Als Beispiel betrachte ich den Streifen

$$1 \leq u \leq x, \quad -\frac{1}{\sqrt{u}} \leq v - u^{1/2} \leq \frac{1}{\sqrt{u}}$$

und ich beweise, dass die Anzahl der Gitterpunkte in diesem Streifen gleich $O\left(x^{\frac{25}{26}}\right)$ ist, während Herr SKOLEM nur zeigt, dass $\frac{A(1, x)}{x}$ bei unbeschränkt anwachsendem x gegen Null konvergiert.

Mathematics. — *Ueber Mannigfaltigkeiten und ihre Abbildungen.* By HANS FREUDENTHAL. (Communicated by Prof. L. E. J. BROUWER.)

(Communicated at the meeting of December 19, 1936.)

In vorliegender Note führen wir in die neuere Homologietheorie eine, wie mir scheint, zweckmässige Symbolik ein, zeigen wir die Isomorphie des Alexanderschen und des Gordonschen Ringes einer Homologiemannigfaltigkeit, ordnen wir den Hopfschen Umkehrhomomorphismus in die neuere Homologietheorie ein und erweitern seinen Gültigkeitsbereich, geben wir eine Simplicialzerlegung des cartesischen Produktes zweier Simplexe an, und betrachten wir gewisse verallgemeinerte Mannigfaltigkeiten.¹⁾

¹⁾ Wir werden den Inhalt dieser Note anderwärts ausführlich darstellen.

1. *Simplexgitter* heie ein System abstrakter absoluter Simplexe, wie es etwa in einem Polytop vorliegt (es werden hier nur endliche Systeme betrachtet); ein abstraktes ϱ -dimensionales Simplex ist dabei als alternierendes Produkt $[a_0 \dots a_\varrho]$ seiner Ecken zu verstehen. Wir erklren formal *untere* und *obere* ϱ -dimensionale Simplexe, t_ϱ und t^e , ferner ein *Produkt* (ohne Zwischenpunkt) $t^e t_\varrho$, das $+1$ bzw. -1 ist, wenn t^e und t_ϱ dieselben bzw. entgegengesetzte Simplexe sind, und das sonst 0 ist. *Untere* bzw. *obere Komplexe*, k_ϱ bzw. k^e , heien die Linearformen in den t_ϱ bzw. t^e mit Koeffizienten aus gewissen Bereichen. Wo von $k^e k_\varrho$ die Rede ist, sollen die beiden Koeffizientenbereiche zueinander mod 1 duale abelsche Gruppen und $k^e k_\varrho$ eine reelle Zahl mod 1 sein, die sich aus den $t^e t_\varrho$ auf Grund von Distributivittsforderungen berechnet. Die k_ϱ bzw. k^e bilden eine Gruppe K_ϱ bzw. K^e . Wo es ntig ist, steht das betreffende Simplexgitter in Klammern hinter k und K .

2. R und S seien zwei Simplexgitter. Ein stetiger Homomorphismus

$$\mathfrak{f} K_\varrho(R) \subset K_\sigma(S)$$

induziert einen stetigen Homomorphismus (in umgekehrter Richtung)

$$K^\sigma(S) \mathfrak{f} \subset K^e(R)$$

auf Grund der Festsetzung

$$k^\sigma(S) (\mathfrak{f} k_\varrho(R)) = (k^\sigma(S) \mathfrak{f}) k_\varrho(R)$$

(es ist dabei zweckmig, wie wir es getan haben, das Funktionszeichen hinter das Argument zu schreiben).

Wichtige Homomorphismen sind: der Homomorphismus, der durch eine simpliziale Abbildung $\mathfrak{f} R \subset S$ induziert wird (er wird auch wieder \mathfrak{f} genannt); die „Unterteilung“ (insbesondere die baryzentrische); die Randbildung r ; der (spter erklrte) Operator \mathfrak{d} .

3. Ein Komplex mit der Eigenschaft $r z_\varrho = 0$ bzw. $z^e r = 0$ heit *unterer* bzw. *oberer Zyklus*. In der blichen Weise gelangt man so zu den unteren und oberen Bettischen Gruppen, B_ϱ und B^e (in dieser Bezeichnung folgen wir A. KOLMOGOROFF statt J. W. ALEXANDER), die, wie man leicht sieht, zueinander dual sind. In bekannter Weise (am bequemsten wohl nach Verf., Compositio Math. 4 (1937)) dehnt man die Definitionen auf kompakte und im Kleinen kompakte Rume aus.

4. Als Ecken der baryzentrischen Unterteilung S von R werden die Mengen a_0, \dots, a_k definiert, fr die $[a_0 \dots a_k]$ ein nichtverschwindendes Simplex darstellt; sie werden mit $a_{0 \dots k}$ bezeichnet; Simplexe von S sind die Eckenfolgen $a_{n_0} \dots a_{n_\varrho}$ mit aufsteigenden Indexmengen $n_0 \subset \dots \subset n_\varrho$.

Liegen die Ecken von R in einer festen Reihenfolge numeriert vor, so lt sich die simpliziale Abbildung $\mathfrak{o} S \subset R$ definieren, die jeder Ecke

$a_{0\dots k} = (a_0, \dots, a_k)$ von S die in der gegebenen Reihenfolge am höchsten stehende unter den Ecken a_0, \dots, a_k von R zuordnet. Diese simpliziale Abbildung wird die Bedeutung verständlich machen, die bei J. W. ALEXANDER die von E. ČECH und H. WHITNEY herrührende Idee der festen Eckenanordnung erhält.

Simplexe, deren Ecken in der gegebenen Reihenfolge angeordnet sind, heißen normal.

5. Für d -dimensionale orientierte Pseudomannigfaltigkeiten R erklären wir den Dualoperator δ

$$\delta[a_0 \dots a_e] = \sum \pi([a_0 \dots a_d]) [a_{0\dots e} a_{0\dots e+1} \dots a_{0\dots e+1\dots d}],$$

der einem Simplex seine Dualzelle zuordnet; π bedeutet hier das Vorzeichen, mit dem das betreffende Simplex im Grundzyklus von R auftritt. δ bildet obere Bettische Gruppen stetig homomorph in untere dualer Dimension ab; bei Homologiemannigfaltigkeiten ist die Abbildung sogar ein Isomorphismus.

Praktischer als δ ist der (was die Bettischen Gruppen anbetrifft, mit ihm übereinstimmende) Operator $\partial\delta$, da er Simplexe von R wieder in Simplexe von R abbildet; wir setzen fest, dass er obere in untere Simplexe abbildet. Man rechnet leicht aus:

$$\partial\delta[a_0 \dots a_e] = \sum \pi(a_0 \dots a_d) [a_e \dots a_d],$$

hierbei sind auf beiden Seiten nur normale Simplexe zugelassen. Damit ist $\partial\delta k^e$, also auch $k_e \partial\delta$ erklärt; man berechnet:

$$[a_e \dots a_d] \partial\delta = \sum \pi([a_0 \dots a_d]) [a_0 \dots a_e]$$

(auch wieder nur normale Simplexe zugelassen).

Bei Homologiemannigfaltigkeiten stellen vorderes $\partial\delta$ und hinteres $\partial\delta$ für die Bettischen Gruppen wesentlich denselben Homomorphismus dar, ebenso vorderes δ und hinteres δ .

Ist A ein Teilpolytop der Homologiemannigfaltigkeit R , so ist $r\delta$ ein Homomorphismus von $B^e(A)$ in $B_{d-e-1}(R-A)$; ist R eine Homologiesphäre, so ist $r\delta$ ein „Isomorphismus auf“. Praktischer als $r\delta$ ist $r\partial\delta$, falls die Ecken von A in der gegebenen Ordnung zuerst an die Reihe kommen.

6. Bei den folgenden drei Arten Produktbildungen werden Koeffizientenbereiche zugrundegelegt, zwischen denen eine stetige Multiplikation besteht:

a. Das Alexandersche Produkt ²⁾ (in Simplexgittern); für normal geschriebene obere Simplexe setzt man (mit Zwischenpunkt)

$$[a_0 \dots a_e] \cdot [a_e \dots a_{e+\sigma}] = [a_0 \dots a_e \dots a_{e+\sigma}];$$

damit ist dies Produkt für obere Komplexe und Elemente oberer Bettischer

²⁾ Annals of Math. (2) 37, 698—708 (1936).

Gruppen definiert (auf Grund üblicher Methoden dann auch in kompakten und im Kleinen kompakten Räumen).

b. Der Schnitt (in Homologiemannigfaltigkeiten) einer Dualzelle und eines unteren Simplexes von R , der in unteren Simplexen der baryzentrischen Unterteilung von R ausgedrückt ist,

$$\partial [a_0 \dots a_\varrho] \times [a_0 \dots a_\varrho \dots a_\sigma] = \Sigma \mp [a_{0 \dots \varrho} a_{0 \dots \varrho} v_1 \dots a_{0 \dots \varrho} v_1 \dots v_{\sigma-\varrho}],$$

wo über alle Permutationen $v_1, \dots, v_{\sigma-\varrho}$ der $\varrho + 1, \dots, \sigma$ zu summieren und für \pm das Vorzeichen der betreffenden Permutation zu setzen ist. Praktischer ist

$$\partial (\partial [a_0 \dots a_\varrho] \times [a_0 \dots a_\varrho \dots a_\sigma]) = [a_\varrho a_{\varrho+1} \dots a_\sigma];$$

für die (unteren) Bettischen Gruppen liefern beide natürlich dasselbe Resultat).

c. Das I. Gordonsche Produkt³⁾ im Auszenraum einer abgeschlossenen Teilmenge der Homologiesphäre, definiert (bis auf Homologien) für untere Zyklen z_ϱ, z_σ

$$z_\varrho \boxtimes z_\sigma = r(k_\varrho \times k_\sigma) \text{ mit } rk_{\varrho+1} = z_\varrho, rk_{\sigma+1} = z_\sigma.$$

Bei der Produktbildung a addieren sich die Dimensionszahlen, bei b die komplementären Dimensionszahlen, bei c die um eins verminderten komplementären Dimensionszahlen.

7. Die Beziehung zwischen a und b hat E. ČECH⁴⁾ festgestellt:

$$(z_\varrho \times z_\sigma) \partial^{-1} = z_\sigma \partial^{-1} \cdot z_\varrho \partial^{-1}$$

oder:

$$\partial (z^\varrho \cdot z^\sigma) = \partial z^\sigma \times \partial z^\varrho.$$

In unserem Aufbau lässt sich die Formel aus der Formel

$$\partial \partial (t^\varrho \cdot t^\sigma) = \partial (\partial t^\sigma \times \partial \partial \cdot t^\varrho)$$

ableiten, die man leicht verifiziert.

Eine ähnliche Beziehung besteht aber zwischen a und c , wenn die Alexandersche Operation in einem Teilpolytop (oder allgemeiner in einer abgeschlossenen Teilmenge) der d -dimensionalen Homologiesphäre und die Gordonsche in der Komplementärmenge ausgeführt wird. Man hat nämlich

$$az^\varrho \boxtimes az^\sigma = a(z^\sigma \cdot z^\varrho),$$

wo a der Homomorphismus aus 5 ist. Diese Formel ergibt sich aus

$$\partial (\partial t^\varrho \times \partial \partial t^\sigma) = \partial \partial (t^\sigma \cdot t^\varrho).$$

Unter den genannten Voraussetzungen sind also die drei genannten Multiplikationen isomorphe Operationen.

3) Annals of Math. (2) **37**, 519—525 (1936).

4) Annals of Math. (2) **37**, 681—697 (1936).

Uebrigens hat sich hierbei auch die Unabhängigkeit der Alexanderschen Produktbildung von der Reihenfolge der Ecke gezeigt.

8. Wir betrachten jetzt eine stetige Abbildung f einer μ -dimensionalen Homologiemannigfaltigkeit M in eine ν -dimensionale, N . Ohne Beschränkung der Allgemeinheit dürfen wir voraussetzen, dass f simplizial ist und die Reihenfolge der Ecken nicht stört. f induziert Homomorphismen

$$f K_e(M) \subset K_e(N), \quad f B_e(M) \subset B_e(N), \\ K^e(N) f \subset K^e(M), \quad B^e(N) f \subset B^e(M).$$

Obendrein hat man aber einen Homomorphismus

$$f^* z^e = \partial^{-1} (f \partial z^e),$$

der gerade in umgekehrter Richtung wirkt:

$$f^* B^e(M) \subset B^{e-\mu+\nu}(N) \\ B_e(N) f^* \subset B_{e+\mu-\nu}(M).$$

Man hat die Relation

$$\partial f^* = f \partial;$$

praktischer ist noch die äquivalente Relation

$$\partial \partial f^* = f \partial \partial,$$

die auch für Komplexe einen Sinn hat.

f^* ist in gewisser Weise eine Umkehrung von f ; für f^* lässt sich nämlich ($\mu \geq \nu$) die *wichtige Beziehung*

$$f^* (z^e f) \sim \gamma z^e \quad (U)$$

beweisen, in der γ den Abbildungsgrad bedeutet.

Es gilt aber mehr: f ist ja für die oberen Bettischen Gruppen nicht nur ein Gruppen-, sondern (wie man leicht zeigt) sogar ein Ringhomomorphismus,

$$(z^e \cdot z^e) f \sim z^e f \cdot z^e f;$$

etwas derartiges kann man von f natürlich nicht erwarten, immerhin gilt aber die *wichtige Beziehung*

$$f^* (z^e f \cdot z^e) \sim z^e \cdot f^* z^e, \quad (V)$$

von der (U) ein Spezialfall ist. (U) und (V) werden mit ähnlichen Methoden wie die früheren Formeln abgeleitet.

Ganz ähnliche Beziehungen hat man im Schnittring; sie folgen aus (U) und (V), wenn man die Ergebnisse von 6 anwendet. Hier ist nicht f , wohl aber f^* ein Ringhomomorphismus, und man hat

$$f (z_e f^*) \sim \gamma z_e, \quad (U')$$

$$f (z_e \times z_e f^*) \sim f z_e \times z_e. \quad (V')$$

Diese Formeln sind nicht neu. Es sind die Formeln des H. HOPFSchen

*Umkehrhomomorphismus*⁵⁾ mit erweitertem Gültigkeitsbereich. Man soll also erwarten, dass \mathfrak{f}^* mit diesem Homomorphismus im Wesentlichen identisch ist. In der Tat ist das der Fall. Beim Beweise braucht man die folgende Tatsache:

(;) bezeichne das Cartesische Produkt der Glieder in der Klammer; \mathfrak{f} sei die Projektion von $(M; N)$ auf N ; dann ist $z_\varrho \mathfrak{f}^* \wr (z_\varrho; M)$. Es ist mir nicht gelungen, diese Tatsache einfacher zu beweisen als mit Verwendung einer Simplicialzerlegung des Cartesischen Produkts zweier Simplexe, die wir in der folgenden Nr. angeben werden.

Auch für den dritten der behandelten Ringe existiert ein Umkehrhomomorphismus: Sind M und N Homologiesphären, A bzw. B abgeschlossene Teilmengen, und hat man $\mathfrak{f}M \subset N$, $\mathfrak{f}A \subset B$, so ist für ein z_ϱ aus dem Komplement von B $z_\varrho \mathfrak{f}^*$ in dem Komplement von A definiert, sobald nur in der Reihenfolge der Ecken die von A und B zuerst kommen. Dieser Umkehrhomomorphismus ist in anderer Weise früher von Verf.⁶⁾ definiert worden. Für ihn gelten Beziehungen, die analog (U') und (V') gebaut sind. Ferner schlieszt man aus (V'), dass für ein z_ϱ aus A und ein $z_{v-\varrho-1}$ aus dem Komplement von B die Verschlingungszahl von z_ϱ und $z_{v-\varrho-1} \mathfrak{f}^*$ mit der von $\mathfrak{f}z_\varrho$ und $z_{v-\varrho-1}$ übereinstimmt.

9. Seien die Ecken des Simplexes t_μ bzw. t_ν mit $0, \dots, \mu$ bzw. $0, \dots, \nu$ numeriert. Wir bilden die Matrix

$$\mathfrak{M}: \begin{array}{cccccc} 00 & 01 & . & . & . & 0\nu \\ 10 & 11 & . & . & . & 1\nu \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ \mu 0 & \mu 1 & . & . & . & \mu\nu \end{array}$$

Wo von einer Ordnung der Elemente von \mathfrak{M} die Rede ist, sei es die lexikographische. *Weg* w in \mathfrak{M} heisse jede Folge lexikographisch angeordneter Elemente von \mathfrak{M} , die mit 00 beginnt, mit $\mu\nu$ endigt, und in der jedes Element rechter oder unterer Nachbar seines Vorgängers ist. $1 + \psi_\beta(w)$ sei die Zahl der Elemente von w in der β -ten Spalte; $\vartheta(w) = \sum \beta \psi_\beta(w)$.

Die Elemente von \mathfrak{M} seien die Ecken des Simplexgitters von $(t_\mu; t_\nu)$; jeder Weg w werde als $(\mu + \nu)$ -dimensionales Simplex $u_{\mu+\nu}(w)$ aufgefasst. Wir setzen

$$(t_\mu; t_\nu) = \sum (-1)^{\vartheta(w)} u(w).$$

Man kann dann beweisen:

$$r(t_\mu; t_\nu) = (r t_\mu; t_\nu) + (-1)^\mu (t_\mu; r t_\nu).$$

Aus dieser Formel kann man ableiten, dass die Definition das gewünschte Resultat liefert. Dass die angegebene Zerlegung wirklich geometrisch zu realisieren ist, muss natürlich auch gezeigt werden.

⁵⁾ Journ. f. r. u. a. Math. **163**, 71—88 (1930).

⁶⁾ Compositio Math. **2**, 163—176 (1935).

10. Wir betrachten jetzt eine R_n -adische Folge⁷⁾ von Homologiemannigfaltigkeiten M_n mit den Abbildungen f_n^m und dem Limes M . Die zugehörigen unteren Bettischen Gruppen bilden eine G_n -adische Folge

$$f_n^m B_\varrho(M_m) \subset B_\varrho(M_n) \quad , \quad m > n,$$

gleichzeitig aber nach 7 eine G_n -ale Folge

$$B_{d_n - \varrho}(M_n) f_n^m \subset B_{d_m - \varrho}(M_m) \quad , \quad m > n,$$

wenn $(f_n^m)^* = f_m^n$ gesetzt wird. Als Limes erhält man also ausser der G_n -adisch erzeugten unteren Bettischen Gruppe von M (die mit der unteren Bettischen Gruppe von M übereinstimmt⁶⁾) noch eine G_n -al erzeugte. Entsprechendes gilt für die oberen Bettischen Gruppen. Man beachte dabei, dass, wenn die Dimensionen der M_n über alle Grenzen wachsen, die G_n -al erzeugten unteren und die G_n -adisch erzeugten oberen Bettischen Gruppen von M als unendlichdimensional zu bezeichnen sind.

Unter Verwendung von (V') kann man in M die übliche Dualitäts- und Schnitttheorie entwickeln; z.B. ergibt sich als Schnitt zwischen einer G_n -adisch und einer G_n -al erzeugten unteren Bettischen Gruppe von M eine G_n -adisch erzeugte.

Hier erhebt sich natürlich die Frage, wann G_n -adisch und G_n -al erzeugte Gruppe zusammenfallen. Das geschieht z.B., wenn die M_n alle von derselben Dimension sind, alle Abbildungsgrade 1 sind und M im Homologiesinne im Kleinen zusammenhängend ist. Aber auch, wenn beide nicht zusammenfallen, kann die G_n -al erzeugte untere Bettische Gruppe Interesse bieten, z.B. gerade in dem Fall, dass die Dimensionen der M_n über alle Grenzen wachsen.

Auch Betrachtungen von der Art des Alexanderschen Dualitätssatzes lassen sich in M anstellen. Eine abgeschlossene Teilmenge von M erscheint in der Entwicklung von M als R_n -adisch entwickelt in eine Folge $A_n \subset M_n$; die A_n darf man als Polytope voraussetzen. So ergibt sich auf Grund des Schlusses von 8 eine Isomorphie zwischen den G_n -al erzeugten oberen Bettischen Gruppen von A und den G_n -adisch erzeugten unteren Bettischen Gruppen des Auszenraumes von A , falls die M_n Homologiesphären sind. Hier interessiert wieder die Frage, wann die G_n -adisch erzeugten unteren Gruppen des Auszenraumes wirklich die gewöhnlichen Bettischen Gruppen sind; nur für den Fall konstanter Dimensionen hat die Frage einen Sinn, und dann lässt sie sich genau wie die erste beantworten. Im Falle über alle Grenzen wachsender Dimensionen hat man sich aber die Frage zu stellen, ob es zweckmässig ist, die G_n -adisch erzeugten unteren Bettischen Gruppen des Auszenraumes als wirkliche Bettische Gruppen aufzufassen. Wir gehen darauf hier nicht näher ein (siehe J. W. ALEXANDER⁸⁾).

⁷⁾ H. FREUDENTHAL, *Compositio Math.* 4 (1937). (Erscheint demnächst.)

⁸⁾ *Proceedings Nat. Acad. USA.* 21, 222—225 (1935).

Mathematics. — *Sur les lacunes d'un polyèdre et leurs relations avec les groupes de BETTI.* By N. ARONSZAJN (Paris). (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of December 19, 1936).

Depuis quelque temps déjà, en réfléchissant sur le problème de trouver une signification topologique directe (et si possible „intuitive”) pour les nombres et groupes de BETTI, je suis arrivé à l'idée que les nombres de BETTI proviennent de la présence dans l'ensemble donné des lacunes d'un certain genre. Cette explication qui est très intuitive dans les cas simples comme p.ex. le cas d'une circonférence dans un plan (où la lacune consiste dans le „trou” déterminé par cette circonférence dans le plan), est déjà moins claire quand la circonférence est considérée dans l'espace euclidien E_3 et devient, de premier abord, tout à fait dépourvue d'un sens intuitif, si la circonférence est étudiée en soi, sans relation avec un espace environnant quelconque. On peut imaginer différentes méthodes pour donner un sens précis à la notion de lacune; les recherches récentes de M. W. HUREWICZ sur l'homotopie et l'homologie ¹⁾ m'ont permis d'en mettre au point une que je crois assez intéressante.

Dans cette note nous allons présenter la méthode en question et les résultats auxquels elle conduit, en l'appliquant aux *polyèdres topologiques*. Nous considérerons dans des travaux ultérieurs les classes d'ensembles plus étendues qui nécessiteront certains changements dans la méthode ²⁾.

En résumé, les résultats auxquels nous arrivons sont les suivants: par définition, un polyèdre connexe (nous ne considérerons que de tels polyèdres, ce qui toutefois ne forme pas une restriction essentielle) est dépourvu de lacunes quand il est un retracte absolu au sens de BORSUK ³⁾. Un polyèdre P de dimension n peut présenter des lacunes des dimensions i allant de $i=2$ jusqu'à $i=n+1$. On peut débarrasser le polyèdre P de ses lacunes en lui joignant de manière appropriée (qui sera décrite plus loin) un certain nombre de cellules i -dimensionnelles ($i=2, 3, \dots, n+1$) ouvertes ⁴⁾. Les lacunes ainsi comblées, P se transforme en un retracte

¹⁾ Comp. W. HUREWICZ, Beiträge zur Topologie der Deformationen, Proc. Royal Acad. Amsterdam, 38, 112, 521 etc. (1935).

²⁾ Toutefois, il est à remarquer que notre méthode s'applique, avec des changements très légers, aux espaces compacts, connexes, de dimension finie et localement contractiles (pour cette dernière notion voir K. BORSUK, Fund. Math. 19, 236 (1932)). Nous nous sommes limité aux polyèdres pour ne pas trop alourdir notre exposé.

³⁾ Pour la définition des retractes absolus voir K. BORSUK, l.c. p. 229.

⁴⁾ Cellule i -dimensionnelle ouverte (ou fermée) = image homéomorphe d'une sphère i -dimensionnelle ouverte (ou fermée).

absolu. Ce résultat peut être obtenu de plusieurs manières; chaque fois les cellules adjointes de dimensions successives seront en certaines relations d'incidence qui permettront de déterminer les groupes de BETTI⁵⁾ correspondants. Dans chaque système de cellules comblant les lacunes d'un polyèdre P , le nombre des cellules i -dimensionnelles (i -cellules) ne peut pas être inférieur à un nombre $N_i = N_i(P)$ appelé *nombre des lacunes i -dimensionnelles de P* . Il y a des systèmes de cellules comblant les lacunes de P , contenant exactement N_i i -cellules, pour $i = 2, 3, \dots, n + 1$. Les N_i sont liés avec les groupes de BETTI de P , notamment: $N_{i+1} = p^i + \mu^i + \mu^{i-1}$, où p^i est le i -ème nombre de BETTI de P et μ^i est le nombre minimum de générateurs du i -ème groupe de torsion de P . La formule précédente n'est valable en général que pour $i \geq 3$; pour $i = 1$, N_2 dépend du groupe fondamental de P ⁶⁾ et pour $i = 2$, on a la formule $N_3 = p^2 + \mu^2 + (N_2 - p^1)$. Ces exceptions s'expliquent par le rôle spécial de la dimension 1, mis en évidence par les recherches de M. HUREWICZ. Relevons encore, comme conséquence immédiate des formules ci-dessus, que la somme $1 + \sum_{i=1}^n (-1)^i N_{i+1} = 1 + \sum_{i=1}^n (-1)^i p^i$ est égale à la caractéristique d'EULER de P .

1. *Quelques notions auxiliaires de la théorie de groupes.* Les groupes que nous considérerons dans la suite seront déterminés par un nombre fini de générateurs et un système de relations⁷⁾.

I. Soit G un groupe multiplicatif quelconque (la traduction de ce qui suit, en langage additif, est immédiate). Comme on sait, toute relation définissant G peut être écrite sous la forme $r = 1$, où r est un certain produit des générateurs. En ajoutant aux relations du groupe G un certain nombre de relations $r_j = 1$, où r_j sont des produits des générateurs et partant, des éléments de G , on obtient un nouveau groupe G' qui est isomorphe au groupe-quotient du groupe G par le plus petit des sous-groupes invariants contenant les éléments r_j .

Il est clair qu'en ajoutant aux relations de G un nombre suffisant K de relations $r_j = 1$, $j = 1, 2, \dots, K$, on obtiendra un groupe G' se réduisant à l'élément 1. Nous dirons alors que les éléments r_j forment une *Q-base* (*quasi-base*) de G ; le plus petit sous-groupe invariant de G contenant tous les r_j se confond alors avec G . Le minimum du nombre d'éléments d'une *Q-base* de G sera désigné par $\mu(G)$. Une *Q-base* dont le nombre d'éléments atteint ce minimum sera dite *minimale*.

$\mu(G)$ est au plus égal au nombre minimum de générateurs de G . Si G est un produit libre de k générateurs, $\mu(G) = k$. Si G' est une image homomorphe de G , on trouve que $\mu(G') \leq \mu(G)$.

II. Soit maintenant G un groupe abélien additif. Les notions de *Q-base* et de *base* sont alors équivalentes et $\mu(G)$ est le nombre minimum de générateurs engendrant G . On sait

⁵⁾ Signalons dès maintenant que tous les complexes, cycles et groupes de BETTI considérés ici, seront construits (sauf avis contraire) avec des coefficients entiers.

⁶⁾ Pour la définition du groupe fondamental voir p. ex. S. LEFSCHETZ, *Topology*, New York 1930, p. 82, ou H. SEIFFERT et R. THRELFALL, *Lehrbuch der Topologie*, Leipzig-Berlin 1934, p. 149.

⁷⁾ Comp. l'exposé de la théorie de groupes dans le livre cité de H. SEIFFERT et R. THRELFALL.

que la structure de G est déterminée par son rang p et par un certain nombre q de coefficients entiers $m_i \geq 2, i = 1, 2, \dots, q$, appelés *coefficients de torsion*, tels que m_i se divise par m_{i+1} . Le groupe G peut être engendré par $(p+q)$ générateurs canoniques g_j formant une base minimale (donc $\mu(G) = p+q$) qui sont liés par les seules relations: $m_i g_{p+i} = 0$, pour $i = 1, 2, \dots, q$ (ceci, bien entendu, en plus des relations $(g_i + g_j) - (g_j + g_i) = 0$ qui assurent le caractère abélien de G). On peut exprimer ce fait en disant que G est une somme directe de p groupes cycliques infinis (engendrés par les $g_j, j=1, 2, \dots, p$) et d'un groupe fini T , appelé *groupe de torsion de G* , qui se décompose en somme directe de q groupes cycliques aux ordres égaux aux coefficients de torsions m_i (ces groupes sont engendrés par les $g_{p+i}, i = 1, 2, \dots, q$).

III. Soit encore un groupe abélien G . Supposons qu'en ajoutant K relations $r_i = 0$ aux relations de G on réduit le groupe G à l'élément zéro. Dans ce cas, il est clair que $K \geq \mu(G) = p+q$ (comp. I et II). On peut démontrer par un raisonnement classique que dans ces conditions il y a, entre les r_i , exactement $K-p$ relations linéaires à coefficients entiers, linéairement indépendantes entre elles.

2. *Adjonction simpliciale d'une i -cellule*⁸⁾. Soient: \bar{D}_i une sphère i -dimensionnelle fermée, D_i son intérieur et S_{i-1} sa surface. Nous considérerons une certaine décomposition simpliciale de \bar{D}_i et désignerons par \bar{D}_i^t un complexe, formé avec les simplexes de $|\bar{D}_i|$, tel que tout sous-complexe K^i de $|\bar{D}_i|$ dont le bord appartient à $|S_{i-1}|$, est de la forme $t\bar{D}_i^i$, où t est un nombre entier. Représentons maintenant simplicialement S_{i-1} sur un sous-polyèdre F du polyèdre P . Transportons ensuite \bar{D}_i de manière que D_i reste étranger à P tandis que les points de S_{i-1} s'identifient avec leurs images dans P ⁹⁾ (plusieurs points de S_{i-1} peuvent venir se confondre avec le même point de P). On obtient ainsi de D_i une i -cellule ouverte C qui sera désignée comme *adjointe simplicialement* ou *s.-adjointe le long de F au polyèdre P* . La frontière de C est F ; sa fermeture $\bar{C} = C + F$. Si la décomposition simpliciale de \bar{D}_i est convenablement choisie, elle détermine une dé-

⁸⁾ Nous emploierons dans la suite les conventions suivantes: si E est un sous-ensemble (ou peut être considéré comme tel) d'un espace bien déterminé, E désigne la fermeture de E . Soit P un polyèdre, donné dans une certaine décomposition simpliciale. $|P|$ signifiera l'ensemble de tous les simplexes formant cette décomposition. Par sous-polyèdre de P on comprendra un ensemble, somme des certains simplexes de P . Par complexe nous comprendrons toujours un complexe algébrique; nous le désignerons par une lettre majuscule munie d'un indice supérieur indiquant sa dimension. Si P est n -dimensionnel, on désignera par P^n un complexe bien déterminé formé des simplexes de P . On dira que K^i est un sous-complexe de $|P|$ ou appartient à $|P|$, s'il est formé avec des simplexes de P . Nous emploierons le terme *frontière* dans le sens de la théorie d'ensembles; la frontière combinatoire d'un complexe K^i sera appelée le *bord* de K^i et désignée par \bar{K}^i . Pour toutes les notions de la topologie combinatoire nous renvoyons au livre de P. ALEXANDROFF et H. HOPF, *Topologie I*, Berlin 1935.

⁹⁾ Dans la notation de M. BORSUK (comp. Fund. Math. 24, 249 (1935)) le résultat de cette opération serait désigné par $\bar{D}_i \overset{\varphi}{+} P$, signifiant la transformation simpliciale de S_{i-1} sur F .

composition de \bar{C} se raccordant à celle de P le long de F . Du complexe \bar{D}_i^i on obtient alors un complexe \bar{C}^i au bord égal à un cycle F^{i-1} de $|F|$. En désignant par P' le polyèdre obtenu de P par l'adjonction de C , on trouve facilement ¹⁰⁾:

1°. Le groupe fondamental $\pi(P')$ de P' est isomorphe au groupe $\pi(P)$ à part le cas où $i=2$. Dans ce dernier cas $\pi(P')$ est isomorphe au groupe qui s'obtient de $\pi(P)$ si l'on ajoute aux relations de $\pi(P)$ la relation $f=1$, où f est un des éléments de $\pi(P)$ correspondant au chemin fermé formé par F (en tant qu'image simpliciale de la circonférence S_1).

2°. Le j -ème groupe de BETTI de P' , $B_j(P')$, est isomorphe au groupe $B_j(P)$, pour tout j sauf pour $j=i-1$ et $j=i$. Pour $j=i-1$, le groupe $B_j(P')$ est isomorphe au groupe qui s'obtient de $B_j(P)$ si l'on ajoute aux relations déterminant $B_j(P)$ la relation $f_{i-1}=0$, où f_{i-1} est l'élément de $B_j(P)$ correspondant au cycle F^{i-1} . Pour $j=i$, $B_j(P')$ est encore isomorphe à $B_j(P)$ sauf quand l'élément f_{i-1} de $B_{i-1}(P)$ satisfait à une relation $tf_{i-1}=0$, avec $t \neq 0$, dans quel cas $B_j(P')$ est isomorphe à la somme directe de $B_j(P)$ et d'un groupe cyclique infini.

En s'appuyant sur les propriétés ci-dessus et les développements du N° 1, on démontre aisément le

Lemme: I. Soient $C_{2,k}$, $k=1, 2, \dots, K$, des 2-cellules *s.-adjointes* au polyèdre P , formant avec P un polyèdre P' dont le groupe fondamental $\pi(P')$ disparaît. Dans ces conditions on trouve que: 1°. $K \geq \mu(\pi(P))$; 2°. $B_1(P')$ disparaît tandis que $B_j(P')$, pour $j \geq 3$, reste isomorphe à $B_j(P)$; 3°. $B_2(P')$ est une somme directe d'un groupe isomorphe à $B_2(P)$ et de $K-p^1$ groupes cycliques infinis, où p^1 est le rang de $B_1(P)$ (= premier nombre de BETTI de P).

II. Soient maintenant $C_{i,k}$, $k=1, 2, \dots, K$, des i -cellules ($i > 2$) *s.-adjointes* à P et formant avec P un polyèdre P' dont le $(i-1)$ -ème groupe de BETTI disparaît. Dans ces conditions on démontre: 1°. $K \geq \mu(B_{i-1}(P))$; 2°. $\pi(P')$ et $B_j(P')$, pour $j < i-1$ ou $j > i$, restent isomorphes respectivement à $\pi(P)$ et à $B_j(P)$; 3°. $B_i(P')$ est une somme directe d'un groupe isomorphe à $B_i(P)$ et de $K-p^{i-1}$ groupes cycliques infinis, où p^{i-1} est le rang de $B_{i-1}(P)$ (= $(i-1)$ -ème nombre de BETTI de P).

3. *Systèmes de cellules comblant les lacunes d'un polyèdre P .* Supposons qu'un système de cellules contenant K_i i -cellules pour $i=2, 3, \dots, m$ ($m \geq 2$), comble les lacunes du polyèdre n -dimensionnel P . En général, les 2-cellules du système seront *s.-adjointes* au polyèdre P avec lequel elles formeront un polyèdre P_2 , les 3-cellules seront *s.-adjointes* à P_2 et formeront avec celui-ci P_3 et ainsi de suite jusqu'aux

¹⁰⁾ On s'appuie ici dans une grande mesure sur le fait que \bar{C} est "simplexartig bis auf F ". Pour cette notion et ses propriétés voir P. ALEXANDROFF et H. HOPF l.c., p. 203, 262 et 263.

m -cellules qui seront s.-adjointes au polyèdre P_{m-1} et formeront avec ce dernier un polyèdre P_m sans lacunes, c'est à dire un retracte absolu ou, ce qui revient au même, un polyèdre P_m dont le groupe fondamental et tous les groupes de BETTI (sauf le 0-ème) disparaissent ¹¹⁾.

Théorème I: Soit \mathfrak{S} un système des cellules $C_{i,j}$, $j=1,2,\dots,K_i$, $i=2,\dots,m$, comblant les lacunes du polyèdre P . En désignant par p^j le i -ème nombre de BETTI de P , par T_j le j -ème groupe de torsion de P et par $\mu^j = \mu(T_j)$ le nombre des coefficients de torsion de $B_j(P)$, on obtient:

(1) Les groupes $\pi(P_i)$ et $B_j(P_i)$, pour $j < i$, disparaissent tandis que les groupes $B_j(P_i)$, pour $j > i$, sont isomorphes aux groupes correspondants $B_j(P)$.

(2) Le groupe $B_i(P_i)$ est isomorphe à la somme directe de $B_i(P)$ et de $\sum_{j=2}^i (-1)^{i-j} (K_j - p^{j-1})$ groupes cycliques infinis.

(3) On a $K_2 \geq \mu(\pi(P))$ et pour $i = 2, 3, \dots, m$

$$K_i \geq \mu^{i-1} + p^{i-1} + \sum_{j=2}^{i-1} (-1)^{i-1-j} (K_j - p^{j-1}).$$

Démonstration. Le polyèdre P_i s'obtenant de P par l'adjonction successive des \bar{j} -cellules avec $\bar{j} \leq i$, on voit, d'après le No. 2, 2⁰, que les groupes $B_j(P_i)$ pour $j > i$, sont isomorphes aux $B_j(P)$. D'autre part, l'adjonction successive des \bar{j} -cellules avec $\bar{j} > i \geq 2$ transforme P_i en P_m qui est un retracte absolu. Il en résulte, en vertu du No. 2, 1⁰ et 2⁰, que $\pi(P_i)$ et $B_j(P_i)$, pour $j < i$, sont isomorphes aux groupes correspondants de P_m et, par conséquent, disparaissent. Ainsi (1) est démontré.

En posant $P_1 = P$, on voit immédiatement que (2) est vrai pour $i = 1$ (la somme Σ disparaît alors, faute de termes). Supposons maintenant que (2) est vrai pour $i = k - 1$ et démontrons le pour $i = k$. P_k s'obtient de P_{k-1} par s.-adjonction de K_k k -cellules, ayant pour effet la disparition du groupe $B_{k-1}(P_k)$ (d'après (1)). Ceci donne, d'après le Lemme du No. 2 (I) et (II), que $B_k(P_k)$ est isomorphe à la somme directe du groupe $B_k(P_{k-1})$, qui est isomorphe à $B_k(P)$ (d'après (1)), et de $K_k - p$ groupes cycliques infinis, le nombre p désignant le rang de $B_{k-1}(P_{k-1})$. En vertu de (2), pour $i = k - 1$, le rang p est égal au rang de $B_{k-1}(P)$, c'est à dire à p^{k-1} , augmenté de $\sum_{j=2}^{k-1} (-1)^{k-1-j} (K_j - p^{j-1})$.

par conséquent, $K_k - p = K_k - p^{k-1} - \sum_{j=2}^{k-1} (-1)^{k-1-j} (K_j - p^{j-1}) = \sum_{j=2}^k (-1)^{k-j} (K_j - p^{j-1})$. Ainsi (2) est complètement démontré.

D'après le Lemme du No. 2, (II), on trouve: $K_i \geq \mu(B_{i-1}(P_{i-1}))$ pour $i > 2$. D'après (2) le groupe de torsion de $B_{i-1}(P_{i-1})$ est isomorphe à T_{i-1} , donc le nombre de coefficients de torsion du groupe $B_{i-1}(P_{i-1})$ est égal à μ^{i-1} tandis que son rang est égal à $p^{i-1} + \sum_{j=2}^{i-1} (-1)^{i-1-j} (K_j - p^{j-1})$. Suivant le No. 1, (II), on obtient ainsi:

$K_i \geq \mu(B_{i-1}(P_{i-1})) = \mu^{i-1} + p^{i-1} + \sum_{j=2}^{i-1} (-1)^{i-1-j} (K_j - p^{j-1})$, ce qui donne la seconde

¹¹⁾ Comp. W. HUREWICZ, l.c., p. 115 et 522.

partie de (3) pour $i > 2$. La première partie de (3) s'obtient directement du Lemme du No. 2, (I), en vertu de (1) (pour $i = 2$). Cette première inégalité de (3) entraîne la deuxième inégalité pour $i = 2$, car $\mu(\pi(P)) \geq \mu(B_1(P))$, $B_1(P)$ étant une image homomorphe de $\pi(P)$, et $\mu(B_1(P)) = \mu^1 + p^1$. Ainsi (3) est entièrement démontré.

Il est clair qu'en posant $K_i = 0$, pour $i > m$, on obtient du système \mathfrak{S} un système de cellules comblant les lacunes de P , contenant formellement de cellules aux dimensions allant jusqu'à un nombre m' aussi grand que l'on veut (évidemment $P_m = P_{m+1} = \dots = P_{m'}$). Pour ce système, les propriétés (1), (2) et (3) restent valables pour tout $i \geq 2$. De la première inégalité de (3) on tire alors:

$$\sum_{j=2}^i (-1)^{i-j} (K_j - p^{j-1}) = K_i - p^{i-1} - \sum_{j=2}^{i-1} (-1)^{i-1-j} (K_j - p^{j-1}) \geq \mu^{i-1},$$

ce qui donne, mis dans la même inégalité où on aura remplacé i par $i + 1$,

$$K_{i+1} \geq \mu^i + p^i + \mu^{i-1} \dots \dots \dots (4)$$

Pour $i = 1$ et $i = 2$, on a d'après (3) des inégalités plus précises: $K_2 \geq \mu(\pi(P))$ et $K_3 \geq \mu^2 + p^2 + [\mu(\pi(P)) - p^1]$. En posant

$$N_2 = \mu(\pi(P)); N_3 = p^2 + \mu^2 + [\mu(\pi(P)) - p^1]; N_{i+1} = p^i + \mu^i + \mu^{i-1}, \text{ pour } i \geq 3, (5)$$

on trouve ainsi

$$K_i \geq N_i, \text{ pour } i = 2, 3, \dots \dots \dots (6)$$

D'après (2), le m -ème nombre de BETTI de P_m est égal à $p^m + \sum_{j=2}^m (-1)^{m-j} (K_j - p^{j-1})$. Ce nombre étant $= 0$ (car P_m est un retracte absolu), on obtient, vu que $p^i = 0$ pour i plus grand que la dimension n de P et que m peut être pris $> n$,

$$1 + \sum_{j=1}^{m-1} (-1)^j K_{j+1} = 1 + \sum_{j=1}^n (-1)^j p^j = \text{caractéristique d'EULER de } P \dots (7)$$

4. *Construction d'un système minimal de cellules comblant les lacunes de P .* Les nombres K_i de i -cellules d'un système \mathfrak{S} sont bornés inférieurement, d'après (6), par les nombres N_i qui ne dépendent que du polyèdre P . Nous allons construire maintenant un système minimal \mathfrak{S}^0 , dans lequel ces bornes inférieures seront atteintes. Un rôle important, dans cette construction, sera tenu par un théorème de HUREWICZ, d'après lequel, si pour un polyèdre P les groupes $\pi(P)$ et $B_j(P)$ pour $j < i$, se réduisent à l'unité respectivement à zéro, alors dans chaque classe d'homologie des cycles i -dimensionnels de P se trouve au moins un cycle étant une image simpliciale du cycle S_i^i formé de la surface sphérique S_i^{12} .

Théorème II: *Il existe un système \mathfrak{S}^0 de cellules comblant les lacunes du polyèdre P , contenant N_i i -cellules, pour $i = 2, 3, \dots, n + 1$.*

¹²⁾ Comp. W. HUREWICZ, l.c., p. 522, I, et surtout la démonstration de I de laquelle notre énoncé résulte immédiatement.

Démonstration. Choisissons dans le groupe $\pi(P)$ une Q -base minimale formée par $N_2 = \mu(\pi(P))$ éléments f_j (comp. No. 1, I). Pour chaque élément f_j choisissons un chemin fermé correspondant $F_{1,j}$. Ce chemin peut toujours être choisi de manière à former une image simpliciale de S_1 . Le long des $F_{1,j}$ on s.-adjoindra alors les 2-cellules $C_{2,j}$ pour $j=1, 2, \dots, N_2$ et le choix des f_j assure (comp. [No. 2, 10]) la disparition du groupe fondamental du polyèdre P_2 obtenu de P par l'adjonction des $C_{2,j}$. P_2 satisfait ainsi à (1) et aussi, d'après le Lemme du No. 2, (I), à (2).

Supposons maintenant que les i -cellules $C_{i,j}$ et les polyèdres P_i sont déjà construits pour $i \leq k$ de manière à satisfaire aux conditions (1) et (2), où on aura remplacé K_i par N_i . D'après (5), la somme $\sum_{j=2}^k (-1)^{k-j} (N_j - p^{j-1})$ est égale à $(N_2 - p^1)$ pour $k=2$ et à μ^{k-1} pour $k \geq 3$. Ceci donne, suivant (2) (où $K_i = N_i$), que le nombre des générateurs canoniques de $B_k(P_k)$, $\mu(B_k(P_k))$, est égal à $p^2 + \mu^2 + (N_2 - p^1)$ pour $k=2$ et $= p^k + \mu^k + \mu^{k-1}$ pour $k \geq 3$, donc dans tous les cas $= N_{k+1}$. Prenons N_{k+1} éléments $f_{k,j}$ de $B_k(P_k)$ formant une base canonique et choisissons dans la classe d'homologie de chacun d'eux une image simpliciale $F_{k,j}^k$ du cycle sphérique S_k^k . La transformation simpliciale correspondante de S_k donne une image $F_{k,j}$. Il est clair d'après No. 2, 2⁰, que les $(k+1)$ -cellules $C_{k+1,j}$, s.-adjointes à P_k le long des $F_{k,j}$, forment avec P_k un polyèdre P_{k+1} satisfaisant à (1). En calculant le rang de $B_k(P_k)$ et en appliquant No. 2, Lemme (II), on trouve que P_{k+1} satisfait à (2), avec $K_j = N_j$.

Vu que $p^i = 0$ pour $i > n$ et que $\mu^i = 0$ pour $i > n-1$, on obtient d'après (1), (2) avec $K_j = N_j$ et (5), que P_{n+1} est un retracte absolu ¹³⁾, donc que les lacunes de P sont comblées par les cellules $C_{i,j}$ avec $j=1, \dots, N_i$, $i=2, \dots, n+1$, c.q.f.d.

Remarque: On peut montrer que les nombres de lacunes N_i , pour $i > 3$, ont la signification suivante dans la théorie d'homologie: N_i est le nombre minimum des complexes K_j^{i-1} aux coefficients entiers tels que K_j^{i-1} est un cycle mod. m_j , pour un $m_j = 0, 2, 3, \dots$, et que tout cycle C^{i-1} construit avec un groupe abélien quelconque \mathfrak{A} de coefficients, est homologue à une combinaison linéaire: $\sum_j a_j K_j^{i-1}$, avec des a_j de \mathfrak{A} .

5. *Tableaux d'incidence, détermination des groupes de BETTI.* Soit \mathfrak{S} un système des cellules $C_{i,j}$, $j=1, 2, \dots, K_i$, $i=2, \dots, m$, comblant les lacunes du polyèdre P . La fermeture $\overline{C_{i,j}}$ (relativement à P_i) s'obtient par une transformation simpliciale de la sphère fermée $\overline{D_i} = D_i + S_{i-1}$ qui représente de manière homéomorphe D_i sur $C_{i,j}$. Nous choisirons l'orientation de D_i et fixerons ainsi l'orientation de $C_{i,j}$. L'image $F_{i-1,j}$ de S_{i-1} , comme sous-ensemble de P_{i-1} , pourra contenir des points de certaines $C_{i-1,k}$. Les points de S_{i-1} aux images appartenant à $C_{i-1,k}$, forment une ou plusieurs régions connexes et l'image de chacune de ces régions couvre $C_{i-1,k}$ un nombre bien défini de fois, ce nombre étant entier, positif, nul ou négatif. Le nombre de ces régions dont les images couvrent $C_{i-1,k}$

¹³⁾ Le cas $n=1$ semble d'abord former une exception, car dans ce cas, d'après (2), $\mu(B_2(P_2)) = p^2 + \mu^2 + (N_2 - p^1) = N_2 - p^1$; mais on sait que pour $n=1$, $\pi(P)$ est un produit libre des p^1 générateurs, donc suivant N⁰. 1, I), $N_2 = \mu(\pi(P)) = p^1$ et $\mu(B_2(P_2)) = 0$.

exactement h fois, $h = \pm 1, \pm 2, \dots$, sera désigné par $A_{j,k,h}^i$. Les nombres $A_{j,k,h}^i$ forment ce que nous appellerons *tableau complet d'incidence du système* \mathfrak{S} . Le *tableau algébrique d'incidence* sera formé par les nombres algébriques d'incidence des $C_{i,j}$ avec $C_{i-1,k}$, donnés par $A_{j,k}^i = \sum_h h A_{j,k,h}^i$.

Si l'on considère les $\bar{C}_{i,j}^i$ comme des cellules au sens large dans une décomposition cellulaire de P_m , on trouve comme relations d'incidence: $\bar{C}_{i,j}^i = Q^{i-1} + \sum_k A_{j,k}^i \bar{C}_{i-1,k}^{i-1}$, où Q^{i-1} est un complexe de $|P|$. Ceci

indique que la considération au point de vue homologique du complexe abstrait formé par les $C_{i,j}$ avec le tableau d'incidence $\{A_{j,k}^i\}$ ¹⁴⁾ est équivalente à l'étude du polyèdre P_m modulo P ¹⁵⁾. D'autre part, P_m ayant tous ses groupes de BETTI (sauf le 0-ème) réduits à 0, on prouve facilement que le $(i+1)$ -ème groupe de BETTI modulo P de P_m est isomorphe au i -ème groupe de BETTI de P , pour $i \geq 1$ ¹⁶⁾. Il en résulte le théorème suivant:

Théorème III: *Le i -ème groupe de BETTI de P , pour $i \geq 1$, est isomorphe au $(i+1)$ -ème groupe de BETTI du complexe abstrait formé par les $C_{i,j}$ avec le tableau d'incidence $\{A_{j,k}^i\}$.*

En ce qui concerne le tableau complet d'incidence nous indiquerons seulement qu'il est en certaines relations avec les groupes d'homotopie¹⁷⁾.

Remarque: Le système minimal \mathfrak{S}^0 du N^0 . 4 peut être construit de manière que: 1⁰. $A_{j,k}^{i+1} = m_k^{i-1}$, pour $i \geq 2$, $j = \mu^i + k$, $k = 1, 2, \dots, \mu^{i-1}$, m_k^{i-1} désignant le k -ème coefficient de torsion du groupe $B_{i-1}(P)$, 2⁰. $A_{j,k}^3 = 1$, pour $j = \mu^2 + \mu^1 + h$, $k = \mu^1 + h$, $h = 1, \dots, [N_2 - (p^1 + \mu^1)]$, et 3⁰. $A_{j,k}^{i+1} = 0$ dans tous les autres cas.

6. *Quelques exemples.* I. Une variété 2-dimensionnelle close et orientable de genre p , présente $2p$ lacunes 2-dimensionnelles et une lacune 3-dimensionnelle. On peut les combler avec des cellules $C_{2,j}$, $j = 1, 2, \dots, 2p$, et $C_{3,1}$, aux incidences $A_{1,j+1}^3 = A_{1,j-1}^3 = 1$, pour $j = 1, 2, \dots, p$, tous les autres $A_{1,j,h}^3$ s'annulant. Les $A_{1,j}^3$ sont tous nuls.

II. La surface sphérique S_n peut être comblée avec une seule $(n+1)$ -cellule.

¹⁴⁾ Pour la notion du complexe abstrait voir A. W. TUCKER, *Annals of Math.* **37**, 92 (1936). Les nombres $A_{j,k}^i$ y correspondent aux nombres $[C_{i,j}^i : C_{i-1,k}^{i-1}]$.

¹⁵⁾ Pour l'homologie modulo un sous-polyèdre voir S. LEFSCHETZ, l.c., p. 17.

¹⁶⁾ Comp. S. LEFSCHETZ, l.c., p. 143, le raisonnement qui y conduit aux relations (13).

¹⁷⁾ Il s'agit ici de différents groupes d'homotopie introduits par W. HUREWICZ, l.c., p. 113, K. BORSUK, *Compt. Rend. Ac. Sc. Paris* **202**, 1400 (1936) et N. ARONSZAJN, *Compt. Rend. Ac. Sc. Paris* **202**, 1475 et 1643 (1936). Remarquons que M. K. REIDEMEISTER a défini des groupes d'homotopie d'un genre différent, voir *Math. Ann.* **112**, 586 (1936).

III. L'espace projectif réel n -dimensionnel présente une lacune de chaque dimension $i = 2, 3, \dots, n + 1$. On peut combler ces lacunes avec des cellules $C_{i,1}$ aux incidences algébriques $A_{i,1}^i$ égales à 0 ou à 2 suivant que i est pair ou impair.

Chemistry. — *Examples of stable unmixing in binary systems: Salt + Water.* By H. G. BUNGENBERG DE JONG and L. W. J. HOLLEMAN. (Communicated by Prof. H. R. KRUYT).

(Communicated at the meeting of December 19, 1936).

In previous communications¹⁾ examples were given of unmixing in aqueous salt solutions which may be regarded as crystalloid analogues of the complex and auto-complex coacervation respectively of biocolloids.

It is to be expected that a closer examination of this unmixing in aqueous salt solutions may lead to a better understanding of coacervation.

It is further a considerable simplification of the theory that already in binary systems: $H_2O + \text{salt}$, if the salt is well chosen, an area of unmixing may be found. A further construction of a t (temperature) — x (composition in percentages by weight) diagram for such an unmixing in the binary system $H_2O + \text{salt}$, however, had to be postponed till experimentally and preparatively we had become acquainted with suitable examples.

In the preceding communication incidentally we described cases of unmixing in mixtures of novocain (p. aminobenzoyl-diethylamino-ethanol-hydrochloride) solutions with solutions of other salts ($K_2Cr_2O_7$, etc.). The unmixed salt-rich layer in most cases easily crystallizes and the product of double decomposition may be purified by recrystallization. In this

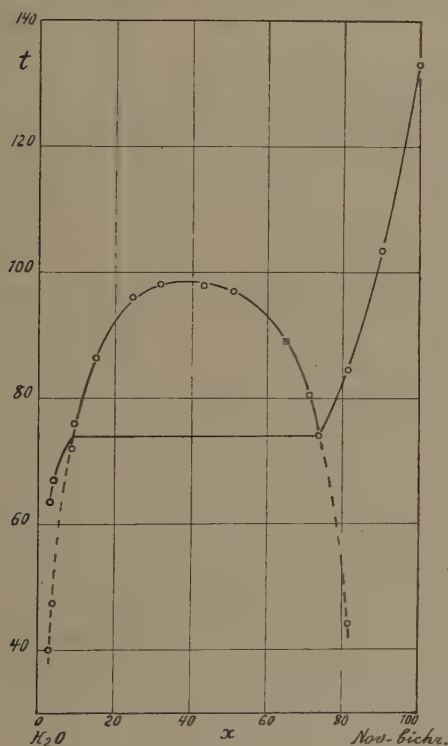


Fig. 1.

way a number of salts of the novocain base were prepared and each time

¹⁾ H. R. KRUYT and H. G. BUNGENBERG DE JONG, Proc. Royal Acad. Amsterdam, **38**, 714 (1935). H. G. BUNGENBERG DE JONG and L. TEUNISSEN—VAN ZIJP, Proc. Royal Acad. Amsterdam, **39**, 1103 (1936).

the presence of the unmixing-area which was to be expected was examined in the binary combinations: Water + Salt.

Now it became apparent that in some of these systems between certain limits of temperature *stable* unmixing occurs, which is important from a theoretical point of view.

As an example follows the t — x diagram of the system water-bichromate of the novocain base (cf. fig. 1 where for the sake of brevity we indicated this salt by Nov.-bichr.).

This salt was prepared by double decomposition of novocain ($C_{13}H_{20}N_2O_2 \cdot HCl$) with $K_2Cr_2O_7$ in aqueous solution and repeated recrystallization of the obtained product out of water. Meltingpoint $133^\circ C$.

Analysis: Found for the content of $H_2Cr_2O_7$: 31.66 and 31.63 % respectively.

Calculated for $(C_{13}H_{20}N_2O_2)_2 \cdot H_2Cr_2O_7$: 31.59 %.

Reaction upon Cl ion negative.

The t — x diagram could be determined in a simple way by so-called "thermic analysis": weighed amounts of the salt and of water in closed ampullae of a volume of 1 cc were slowly heated in a water- or paraffin-bath.

At a rise of temperature, at 74° , the systems, the composition of which lies between 9 and 74 % of salt, so e.g. the 50 % mixture, change from the condition: crystals in equilibrium with saturated solution into two co-existing liquids (the crystals "melt under water") and become homogeneous only at a higher temperature.

The latter temperature may also be determined, starting from the homogeneous system, at a decreasing temperature. The disappearing and setting in respectively of a distinct turbidity was regarded as a criterion for the unmixing-temperature. The points of the unmixing-curve thus found, which indicates the composition of the co-existing liquids at each temperature, are all determined to 0.5° accurately.

At temperatures below 74° , where stable equilibria are only possible between crystals and saturated solution, nevertheless metastable unmixing may be easily realized. For this purpose the system is first heated till above the temperature at which the last crystals disappear (i.e. the saturation-temperature of the crystals at the given total composition of the system, which can be determined a little less accurately than the unmixing-temperatures) and then cooled. Crystallization usually does not occur then and in this way the unmixing-curve may be determined also in the metastable area. The changes in pressure on heating of the closed system, which besides contains a gas-phase, may be left aside as being of minor importance to the equilibria in the condensed system. Similar unmixing-areas undoubtedly exist also in the systems: water-perchlorate or rhodanide of the novocain base.

For the theory of the complex and auto-complex coacervation respectively the cases discussed here are of importance, for in case of coacervation

it seems that we have to deal with a stable unmixing. In how far this is indeed stable and does not remain to exist only as a result of an insufficient formation of crystal-germs or (and) of a too small crystallization velocity can of course not be decided as long as the expected crystalline "colloid-colloid salts" (e.g. gelatin-arabinate) are not yet known.

Between the complex coacervation and the analogous unmixing in crystalloid salt solutions thus far the apparently fundamental difference existed that in the latter case the analogous inter-relation between the two oppositely charged ions only seemed to allow metastable unmixing, i.e. where the "coacervate" was only passed as a transition-stage to the stable ordered-crystalline condition.

In the examples described here the unmixing above certain temperatures is indeed stable and the fundamental difference which we considered still present between complex coacervation and its crystalloid analogue consequently does not exist.

Leiden, December 1936.

Chemistry. — *The spreading of Protamine Insulinate.* By E. GORTER and L. MAASKANT. (From the Laboratory of the Children's Hospital of the University of Leiden, Holland.) (Communicated by Prof. J. VAN DER HOEVE.)

(Communicated at the meeting of December 19, 1936).

It is possible to combine the insulin with some basic group, so that the combination has its iso-electric point nearer to the p_H of the tissue fluid than insulin.

By combining the usual insulin hydrochloride (in solution p_H = about 2.5) with a protamine a compound is formed, which has its point of minimum solubility at about the p_H of the blood serum.

H. C. HAGEDORN, B. NORMAN JENSEN, N. B. KRARUP, J. WODSTRUP NIELSEN ¹⁾ prepared a special insulin preparation which is absorbed more slowly and, therefore, has a more gradual effect than ordinary insulin. This "Leo Insulin Retard" is manufactured by the "Nordisk Insulin Laboratorium".

We have now studied the spreading of Leo Insulin Retard and an insulin-clupein complex, made by us.

GORTER and VAN ORMONDT ²⁾ showed that insulin is a very well-spreading substance. This protein shows a slightly diminished spreading at the acid side of the iso-electric point, which proves that the tendency to spread in a charged condition of the protein is high.

GORTER and his collaborators ³⁾ studied the spreading of artificially

¹⁾ Journ. Am. Med. Assn. Vol. 106 (1936).

²⁾ Proc. Royal Acad. Amsterdam, 36, 922 (1933).

³⁾ E. GORTER, H. VAN ORMONDT, TH. M. MEYER, Biochem. J. 29, 38 (1935).

prepared complex proteins of different types in order to prove the correctness of the supposition, that the type of the p_H -area curve depends on the ionizable groups.

We mentioned already, that insulin can be combined with a protamine.

It is obvious that the latter, being a basic substance must combine with the free COOH groups of the insulin. When studying the spreading of this complex protein, we see no change at the acid side of the iso-electric point, whereas the minimum on the alkaline side disappears completely (see fig. 1). This figure shows, that the spreading measurements of these two complex proteins agree. The amount of the protamine in these complex proteins is small (1 : 10). Moreover the protamines themselves belong to that class of proteins, which do not spread owing to the too great solubility in the solutions used.

In order to study the effect of p_H on the amount of the spreading we used: dilute hydrochloric acid solutions between 1 and 3, a $1/300$ molar sodium acetate-acetic acid solution between p_H 3.6 and 5.5 and $1/300$ molar veronal-acetate buffer solutions according to MICHAELIS between p_H 5.5 and 7.5.

We have also made turbidity measurements in $1/300$ mol. phosphate

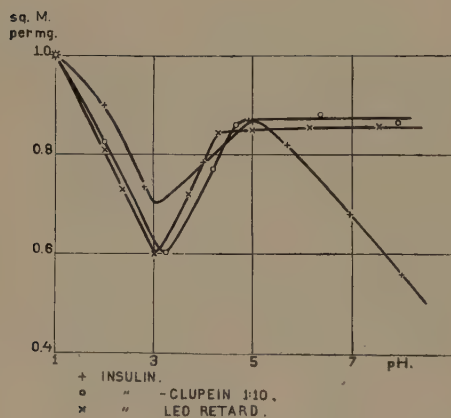


Fig. 1.

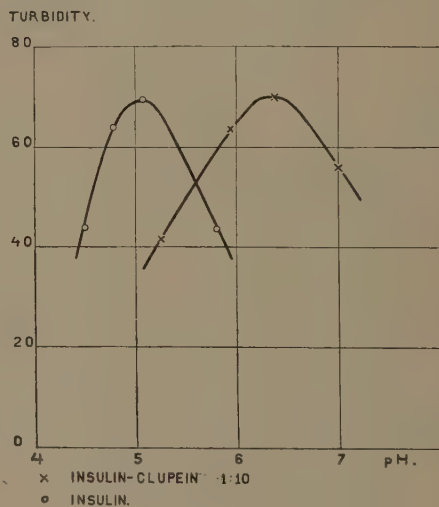


Fig. 2.

buffer solutions of the insulin-clupein complex, which show that the point of minimum solubility approach the p_H of the blood serum (see fig. 2).

These spreading experiments give also an explanation of the fact, that these insulin protamines have a more gradual effect, when injected in the body as the insulin.

We have made use of insulin of a pure preparation from „N.V. Organon” at Oss (Netherlands). To control the purity of the insulin this

substance was recrystallized after D. A. SCOTT¹). There was no change in purity after the recrystallization.

The clupein was prepared according to KOSSEL²), from the sperm of the herring. The testicles are put through a mincing machine and the pulpy mass suspended in 4 or 5 volumes of water. The milky liquid is treated with dilute acetic acid until strongly acid to congo red. After filtering the precipitate is extracted with alcohol and ether. About 20 grams of the remaining white floury mass are shaken for half an hour with 100 cc 1 per cent sulphuric acid and filtered. The sulphuric acid extract is precipitated with three volumes of alcohol and the precipitate, consisting of the protamine sulphate, collected, dissolved in a little hot water and reprecipitated with alcohol. Further purification was effected by treating a warm aqueous solution of the protamine sulphate with sodium picrate. Clupein was obtained as the free base by treating the aqueous solution of the sulphate with baryta.

Insulin with clupein.

A solution of insulin in hydrochloric acid ($p_H = 2.5$), containing 5 mg. insulin per ml. was prepared and 2 cc. of this solution was mixed with 0.1 cc. of a clupein solution, containing 10 mg. clupein per ml.

Summary.

The spreading of Leo Insulin Retard and an insulin-clupein complex was studied in comparison with the results of the spreading of insulin. These experiments show, that the minimum on the alkaline side of the insulin p_H -area curve disappears completely, when this protein is combined with a protamine.

¹) J. of Biol. Chem., **92**, 281 (1931).

²) A. KOSSEL, The protamines and histones, p. 19.

Chemistry. — *The spreading of urease and Bence-Jones protein.* By E. GORTER and L. MAASKANT. (From the Laboratory of the Children's Hospital of the University of Leiden, Holland.) (Communicated by Prof. J. VAN DER HOEVE.)

(Communicated at the meeting of December 19, 1936).

We have now studied the spreading of two other proteins and examined the influence of the p_H of the solution in the tray on the spreading of urease and Bence-Jones protein.

The general rule is, that the spreading is maximal at the iso-electric

point and when the reaction of the solution is strongly acid and alkaline, whereas on both sides of the iso-electric point there are found minima.

The urease and Bence-Jones protein show compared with other proteins a same deviation in this way, that the spreading measured after 1 minute on the p_H of the iso-electric point is small, while the spreading increases after a long time.

In order to make a conclusion about the position of the iso-electric point of these proteins according to the spreading method, it was necessary to study the influence of time on the amount of spreading at different p_H .

So we could make a comparison with the iso-electric points of urease and Bence-Jones protein found in the literature and measured in a different way from the spreading method.

For these spreading measurements dilute hydrochloric acid solutions between p_H 1 and 3, a $1/300$ molar sodium acetate-acetic acid solution between p_H 3.6 and 5.5, and $1/300$ molar veronal acetate buffer solutions according to MICHAELIS between p_H 5.5 and 7.3 were used.

Bence-Jones protein.

This substance, suspended in a solution of ammonium sulphate, was kindly placed at our disposal by Prof. MAGNUS LEVY of Berlin.

The Bence-Jones protein was centrifuged, washed with small amounts of cold water and dissolved in a physiological salt solution.

The protein concentration was about 5 milligram per cc. In fig. 1 the

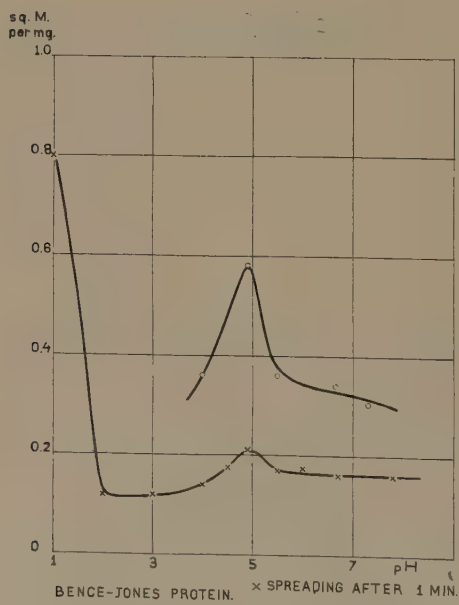


Fig. 1.

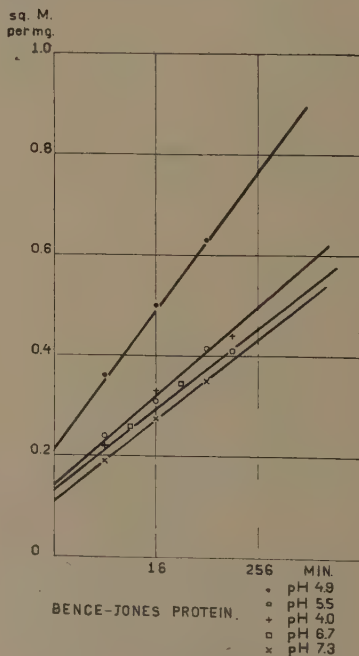


Fig. 2.

measured spreading after 1 minute is plotted against the p_H of the solution in the tray on which the substance is spread. It appears that the protein spreads only maximal on a solution of a $p_H=1$ and that the spreading is small on less acid solutions. At about the p_H 5 the spreading increases somewhat. Fig. 2 shows the influence of time on the spreading of Bence-Jones protein at different p_H values.

The curves in Fig. 1 show, that the iso-electric point of our Bence-Jones protein lies at about p_H 4.9.

It appeared to MC FARLANE¹⁾ that the Bence-Jones protein does not always refer to the same substance, but that urinary protein of varying composition can give the characteristic Bence-Jones reactions.

Several iso-electric points of the B.-J. protein are mentioned in the literature: 4.0—4.25²⁾; 5.2¹⁾; 6.56¹⁾. It appeared to F. MAINZER³⁾, that the iso-electric point of denatured B.-J. protein is at p_H 4.9.

Urease.

The urease crystals, kindly send to us by Prof. W. T. ASTBURY and prepared by J. B. SUMNER were suspended in acetone. It was rather difficult to prepare a solution from the crystalline material, that was very active and could be induced to spread.

We succeeded at last by collecting the crystals by centrifugal force and dissolving them in a small amount of very pure redistilled water⁴⁾. A small part of the crystals went into solution. After eliminating the non-dissolved substance by centrifugal force the activity of the solution was examined. Its activity was tested by adding 1 cc. of the urease-solution, containing 3.5 mgr. urease, to a ureum-phosphate buffer mixture (6.8 % Na_2HPO_4 , 4.2 % K_2HPO_4 and 3 % ureum; $p_H=6.9$). 120 mgr. ammonium nitrogen were liberated in half an hour. The ammonia, that has been formed was determined by the aeration method. We have used the method of VAN SLYKE and CULLEN⁵⁾ followed by titration with 0.01 N NaOH, methyl red being used as indicator.

After 24 hours standing the activity of the aqueous solution of urease had diminished to half its strength. The p_H had a distinct influence on the size of the spreading, measured after one minute (fig. 3). Fig. 4

1) Bioch. J., Vol. XXIX, N^o. 5, pag. 1205 (1935).

2) O. JERVELL and R. NICOLAYSEN, Bioch. Z. 250, 308—311 (1934).

3) Bioch. Z. 246, 156—163 (1932).

4) J. B. SUMNER and D. B. HAND (Journ. Biol. Chem. 76, 151, 1928) discovered, that the destructive effect of distilled water on the activity of urease is considerably diminished if the water is redistilled from glass.

5) D. D. VAN SLYKE and G. E. CULLEN, Journ. Biol. Chem. 19, 211 (1914); Ibid., 24, 117 (1916).

shows, that the time has a great influence on the size of the area at the iso-electric point $p_H=5$.

J. B. SUMMER and D. B. HAND¹⁾ found, that the curves obtained by precipitating urease with a phthalate buffer and with lead acetate cross at

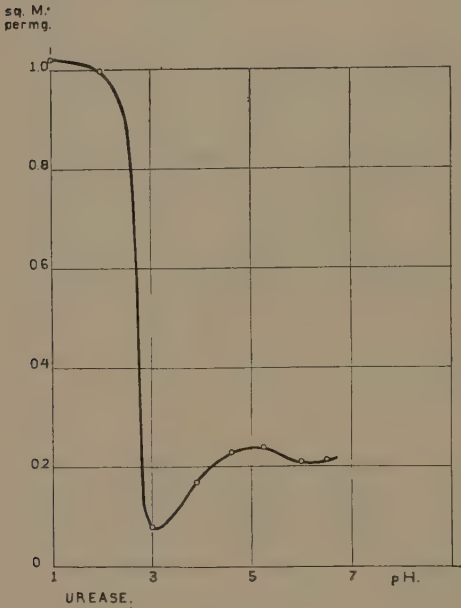


Fig. 3.

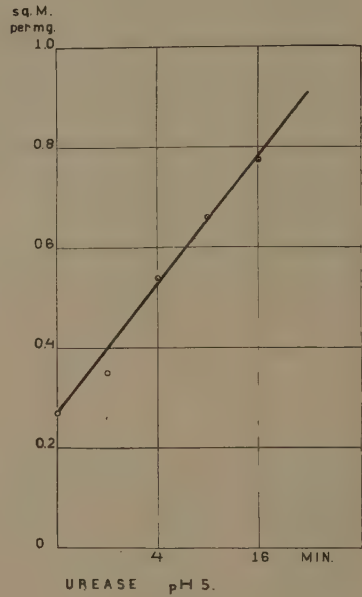


Fig. 4.

p_H 4.95 and they indicated this p_H as the probable iso-electric point of urease. This result agrees also with our determination of the iso-electric point of urease according to the spreading method.

¹⁾ Journ. Biol. Chem. 78, 34 (1928).

Medicine. — *The action of medicines on auricular fibrillation. II. The action of hydroquinidine, quinidinum purissimum, hydroquinine and quininum purissimum on auricular fibrillation.* By S. DE BOER and A. BROUWER. (Communication from the Pharmacological Laboratory of the University of Groningen.) (Communicated by Prof. E. D. WIERSMA.)

(Communicated at the meeting of November 28, 1936.)

Since WENCKEBACH (1) reported two cases of auricular fibrillation which were cured by quinine, and since FREY (2) found in 1918 that with approximately half of the patients with auricular fibrillation this abnormal auricular activity can give place, through the administration of quinidine, to normal auricular systoles, this remarkable therapeutical action of the quinine alkaloids has had the constant attention of clinicists and experimenters.

A new light seemed to have been thrown on this question by the investigations of Dr. HOLTKAMP (3) and Dr. SANCHES (4). HOLTKAMP found in his experiments, which he carried out on cats, that hydroquinine and hydroquinidine exert a much better antifibrillation action than quinine which contains no hydroquinine and quinidine from which the hydroquinidine has been removed.

A dissertation by Dr. SANCHES (4) was published by the Utrecht Laboratory for Pharmacology. Dr. SANCHES ascribes the favourable action of quinidine to hydroquinidine occurring (present) in it (20 %), whilst according to him the quinidinum purissimum has no effect on auricular fibrillation.

As this question is of great importance, and the results of Dr. HOLTKAMP and Dr. SANCHES did not agree sufficiently well, we again resumed this investigation. We again performed our investigations on cats, leaving the vagi and accelerantes intact.

Method.

Artificial respiration was applied under ether narcosis, the heart being exposed and the pericardium opened (1). Each of the two auricles was then connected with the secondary coil of an induction apparatus, whilst a Pohl's commutator was connected up. In the primary circuit a 4-volt

1) The amounts of ether used by us had no influence on the auricular fibrillation.

accumulator was inserted. The minimum faradic stimulation (duration approx. 3 secs.) was then determined, it being still possible to cause fibrillation. At the same time the minimum faradic stimulation was determined with which after-fibrillation set in. 5 mgr. quinine alkaloid per kg. cat was then injected into the vena saphena, and the determinations were repeated. Every 5 minutes after this a similar quantity was injected, the above-mentioned determinations being repeated each time. This was continued until the frequency of the heartbeat had fallen below 40 per minute. The experiments were in each case performed on both auricles successively.

Results.

The results of all these experiments are given in the tables below. For each of the two auricles the minimum dose is shown at which no fibrillation occurred, and also that at which there was no further after-fibrillation.

Hydrochloridum hydroquinidinae.

Date	Right auricle		Left auricle	
	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs
4—9	10	15	20	25
5—9	10	15	10	15
7—9	15	20	20	20
7—9	10	15	15	20
8—9	20	30	30	30
12—9	20	25	30	30
29—9	20	20	20	20
12—10	40	40	40	40
13—10	45	50	50	55
13—10	5	10	10	15
14—10	10	15	15	15
15—10	20	20	20	45
16—10	15	15	15	20
17—10	20	20	20	25
19—10	15	30	25	30

Hydrochloridum quinidinae purissimum.

Date	Right auricle		Left auricle	
	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs
11—9	15	30	20	30
11—9	15	25	25	25
14—9	10	15	15	15
14—9	15	25	25	25
15—9	15	20	15	25
15—9	15	25	25	30
28—9	15	20	15	25
28—9	15	25	25	25
29—9	20	35	30	35
30—9	15	30	15	15
3—10	15	30	30	30
9—10	20	25	25	25
10—10	15	30	20	30
10—10	15	20	15	25
12—10	15	20	20	35
13—10	5	15	5	15
27—10	10	15	15	15
28—10	20	25	25	25
29—10	30	35	35	45
30—10	20	35	35	35
31—10	10	25	10	25

In order to obtain to some extent comparable values for the four substances of this investigation we calculated the averages of the figures of these four tables.

For the various substances these averages are printed in the table of page 81.

We both, by arrangement, performed part of the experiments of each series, whilst at my request my assistant, Dr. SIEMELINK, also carried out

Hydrochloridum hydroquininae.

Date	Right auricle		Left auricle	
	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs
26—8	20	25	35	40
27—8	30	35	35	45
1—9	15	30	35	40
2—9	15	15	15	15
2—9	25	30	50	55
3—9	20	40	25	50
9—9	25	35	35	35
10—9	20	25	30	40
16—9	30	30	30	35
17—9	30	45	40	45
8—10	45	75	55	70
12—11	45	125	65	125
16—11	15	40	15	50
17—11	40	45	40	50
17—11	35	60	55	75

Hydrochloridum quiniinae purissimum.

Date	Right auricle		Left auricle	
	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs	Minimum dose with which no after-fibrillation occurs	Minimum dose with which no fibrillation occurs
16—9	20	20	25	30
16—9	10	35	35	40
17—9	5	25	15	25
21—9	5	10	10	20
22—9	10	25	25	25
29—9	20	35	30	35
30—9	15	30	15	15
13—11	55	95	75	100
14—11	15	30	25	35
16—11	50	75	75	100

Hydroquinidine.

Right auricle		Left auricle	
Average minimum dose with which no after-fibrillation occurs	Average minimum dose with which no fibrillation occurs	Average minimum dose with which no after-fibrillation occurs	Average minimum dose with which no fibrillation occurs
18.3	22.6	22.6	27

Chinidinum Purissimum

15.5	25	21.1	26.4
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Hydroquinine

27.3	43.6	26.7	36.6
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Chininum Purissimum

20.5	38	33	42.5
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some experiments, without knowing what substances he was working with, and without being acquainted with the literature on the subject.

If, then, we look at these latter tables, we at once see that hydroquinidine has no stronger an effect on auricular fibrillation than quinidinum purissimum, and that hydroquinine has no stronger an effect on auricular fibrillation than quininum purissimum. In view of the comparatively small differences we refrain as yet from concluding that quinidinum purissimum has a stronger effect on auricular fibrillation (counteracts auricular fibrillation more strongly) than hydroquinidine, or that quininum purissimum has a stronger effect on (more strongly counteracts) auricular fibrillation than hydroquinine. Further experiments will be carried out on this subject.

Conclusions.

A further detailed investigation has shown the determinations previously made and the conclusions (3 and 4) drawn therefrom to be incorrect. It has now been found that the action of hydroquinine in cases of auricular fibrillation is no stronger than that of quinine, and that of hydroquinidine no stronger than that of quinidine.

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- Chinidin zur Bekämpfung der absoluten Herzunregelmässigkeit (Vorhofflimmern). D. Arch. f. klin. Med. 136, 70 (1921).

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Chemistry. — *Aging of Fresh Precipitates in Contact with a Liquid Medium. The Irreversible Flocculation of Colloids.* By I. M. KOLTHOFF. (Communicated by Prof. H. R. KRUYT).

(Communicated at the meeting of December 19, 1936).

The term "aging" is a collective name, including all changes which occur in a precipitate after its formation. In a systematic study of the aging of freshly prepared precipitates it is necessary to distinguish between various types of aging which may occur simultaneously, although, as a rule, one or only a few predominate. The following types of aging are considered in this paper:

1. *Perfection* of the highly imperfect particles of the primary precipitate as a result of recrystallization. (Fig. 1, I). This type of aging occurs quite generally, and, as a rule, is particularly pronounced during the early stages.

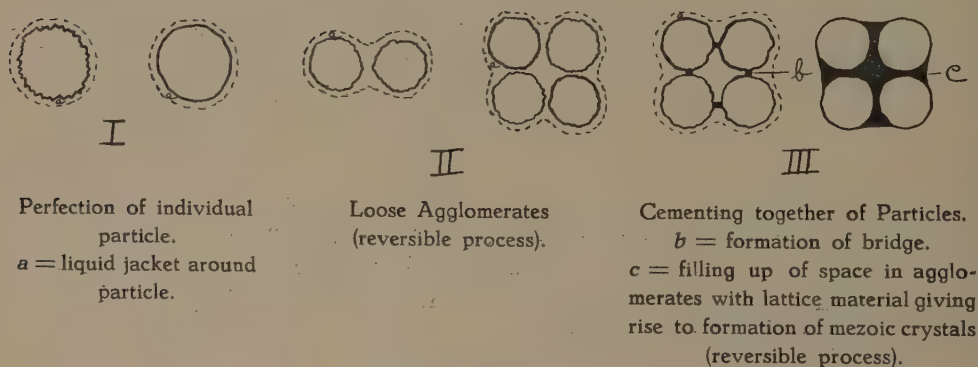


Fig. 1.

2. *Agglomeration* of the particles of the primary precipitate by sharing of their water jackets (Fig. 1, II). This kind of aging may be entirely reversible (peptization) and does not involve a change of the total surface, when the latter is measured by means of a dye which is strongly adsorbed.

As a result of a decrease of the interfacial tension by the adsorbed dye, the loose agglomerates are again dispersed into their primary particles. From an analytical viewpoint it is of interest to mention that the filterability of a precipitate is greatly improved by the formation of these loose agglomerates.

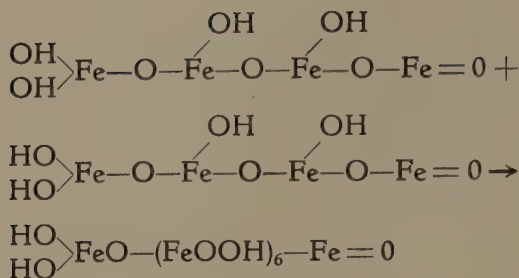
3. *Cementing* together of the particles in the agglomerates as a subsequent result of the perfection (comp. sub. 1). Lattice material may deposit (crystallize out) in the interstices between the primary particles, which are filled with liquid, thus giving rise to the formation of solid bridges. (Fig. 1, IIIC). When the entire space is filled up with lattice material (Fig. 1, IIIC) the crystalline aggregates will have a mozaic structure. The cementing process is irreversible and results in a decrease of the total surface as measured by the dye adsorption. Factors which promote the perfection process (1) will also promote the cementing process (3). A direct cementing together of crystalline particles with ionic lattices as a result of the negative ions in the surface of one particle being attracted by the positive ions of the other¹⁾ — hence without cementing material — does not seem very probable.

4. *Ostwald Ripening*. Of a heterodisperse precipitate the smaller particles with the greater solubility go into solutions and the larger particles grow at the cost of the small ones. This process is usually referred to as "Ostwald ripening" and has always been considered as the most important type of aging. In the following, however, experimental evidence will be presented showing the relative unimportant part played by the Ostwald ripening, when the aging occurs at room temperature. Its contribution to the total aging process is so small compared to that of the perfection, that it may be neglected. This is no longer true when the aging is carried out at higher temperatures for long periods of time, and possibly even at room temperature when the solubility of the solid is relatively great.

5. *Polymerization* of the primary particles. This is a specific case and may occur when the primary, amorphous particles are highly reactive and of such a nature that they react with one another in a chemical way. An example of this kind is found in the aging of hydrous ferric oxide precipitates (ortho ferric hydroxide). In the early stages of aging two molecules of the ortho hydroxide, according to KRAUSE²⁾ react to form a polymerization product containing 8 atoms of iron.

¹⁾ K. FAJANS and VON BECKERATH, Z. physik. Chem. **97**, 478 (1921).

²⁾ A. KRAUSE, Z. anorg. allgem. Chem. **176**, 398 (1928); KRAUSE and M. CIKOWNA, ibid. **204**, 20 (1932); KRAUSE, Z. CZAPSKA and J. STOCK, ibid. **204**, 386 (1932); KRAUSE and A. LEWANDOWSKI, ibid. **206**, 328 (1932); KRAUSE and H. TORNÖ, ibid. **211**, 98 (1933); KRAUSE e.a., ibid. **219**, 213 (1934); KRAUSE, Kolloid Z. **72**, 18 (1935).



More molecules of the ortho hydroxide can be added and finally conglomerates with a chain structure are formed containing 40—50 atoms of iron. Although there is a definite ordering in these conglomerates they are not yet crystalline. The polymerization is accompanied by a dehydration and a change of color. The aging may result in the formation of yellow amorphous ferric acid with a ring structure and finally in the formation of crystalline goethite. The speed and even the kind of aging is greatly dependent upon the composition of the aging medium.

The polymerization is a typical chemical aging contrary to the other types discussed which involve physical processes. This kind of aging does not necessarily involve marked changes of the surface as measured by the adsorption of dye.

6. *Transformation of metastable form of a precipitate* into another metastable or a stable modification. A recrystallization of this nature occurs in specific cases only; when the primary precipitate consists of a metastable form. For example, when calcium oxalate is precipitated at room temperature, it consists partly of higher hydrates (second and third hydrate) and is more or less rapidly transformed into the stable monohydrate. It has not been established yet whether the liquid medium in which the precipitate is aged has an effect upon the speed of transformation. It is to be expected that the transformation is favored by greater solubility in the aging medium.

Perfection of the Primary Particles. Extensive investigations on the aging of lead sulfate precipitated at room temperature from 0.1 molar lead nitrate and 0.1 molar sodium sulfate have been carried out by KOLTHOFF and ROSENBLUM³⁾. The speed of distribution of thorium *B* throughout the solid phase, upon shaking of a radioactive standard lead solution with a definite amount of lead sulfate, was found to be an excellent indicator of the progress of the perfection process. The change of the total surface of the precipitate upon aging was found from the amount of wool violet adsorbed in the saturated surface. Microscopic investigation revealed that the fresh, highly imperfect precipitate was definitely microcrystalline (dendrites; 1—5 microns in length, 0.5—1 micron in width) the individual

³⁾ I. M. KOLTHOFF and CH. ROSENBLUM, J. Am. Chem. Soc. **56**, 1264, 1658 (1934); **57**, 597, 607, 2573, 2577 (1935); **58**, 116, 121 (1936).

crystals having a great tendency to aggregate into large clusters; after a relatively short time of aging it was difficult to measure the individual particle size. X ray photographs revealed that the fresh precipitate had crystallized to form the stable modification; from the diffuseness of the lines it could be concluded that the crystals were imperfectly ordered.

From the results of experiments with thorium *B* it was concluded that especially during the early stages of the aging (first hour or so) a very fast perfection process occurred without being accompanied by pronounced changes of the total surface (dye adsorption). This perfection process is a result of recrystallization. It was found that all factors which decrease the solubility of lead sulfate decrease the speed of recrystallization, and, hence, also of perfection: and conversely, all factors which increase the solubility promote recrystallization and perfection. A layer of adsorbed wool violet on the precipitate prevented recrystallization and therefore, also perfection. When kept in the airdried state at relative humidities of 0.6 or smaller, no aging occurred. These and other experiments showed conclusively that the perfection is a result of recrystallization. From the fact that the specific surface decreased only slightly (fresh precipitate in very dilute lead nitrate: 2.65 mg. Pb p. lg PbSO_4 ; after 1 hour 2.3; after 16 hours 1.74) it was concluded that the Ostwald ripening did not play an important part. Other indications ³⁾ were also obtained that the recrystallization, leading to the perfection, mainly occurs in a liquid layer around the particle. Recently, conclusive evidence to be published in the near future has been obtained by G. NOPONEN ⁴⁾ that during the early stages of aging of freshly precipitated barium sulfate in an excess of barium nitrate no Ostwald ripening occurred, whereas a pronounced perfection took place. From a few figures given in the following table, it is evident that the specific surface as measured with wool violet hardly changes during the first 24 hours of aging in 0.005 M. barium nitrate; hence neither Ostwald ripening nor cementing together has occurred. The decrease of the specific surface found on aging in 0.005 M. sodium sulfate will be discussed below.

TABLE I. *Specific Surface of BaSO_4 obtained from 0.1 M. barium nitrate and 0.1 M. sodium sulfate (order of mixing immaterial)*

Time of aging in hours	Wool Violet absorbed on saturated surface in mg p. lg. BaSO_4	
	Aged in 0.005 M. $\text{Ba}(\text{NO}_3)_2$	Aged in 0.005 M. Na_2SO_4
Fresh	37	37
1	37	28.5
24	42	13.2

⁴⁾ Doctor's thesis, University of Minnesota. June, 1936.

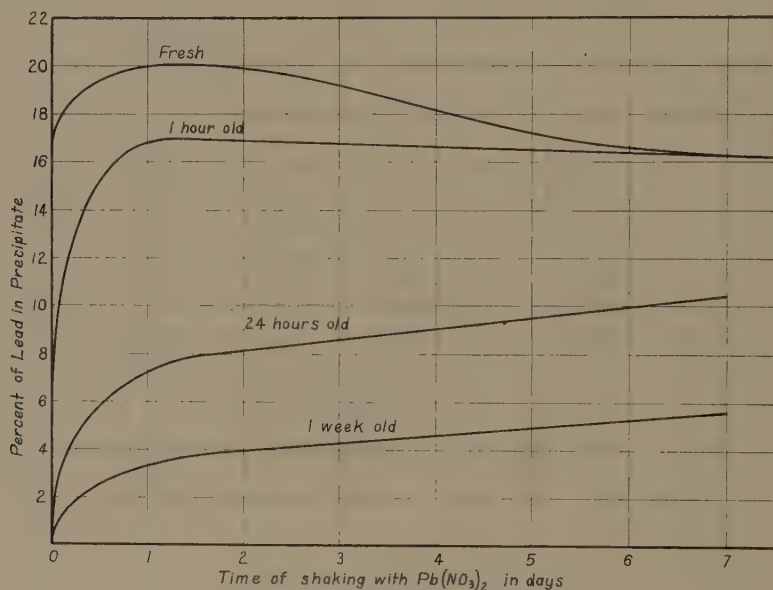
In spite of the fact that the specific surface hardly changed upon aging in 0.005 M. barium nitrate for 24 hours it could be shown that a distinct perfection occurred during this period of time. Instead of using the speed of distribution of a radioactive isotope as an indicator of the perfection process, NOPONEN determined the speed of mixed crystal formation of barium sulfate with lead sulfate when barium sulfate was shaken in the presence of an excess of barium nitrate with lead nitrate



When the suspension contained an excess of sulfate the speed of mixed crystal formation of barium sulfate with barium chromate was found to be a simple, but reliable indicator of the perfection process:



From the results plotted in Fig. 2 it is clearly seen that the speed of "penetration" of the lead into the barium sulfate is much smaller after



Speed of penetration of lead into BaSO_4



To 25 ml. of 0.11 M. $\text{Ba}(\text{NO}_3)_2$ were added 25 ml. of 0.1 M. Na_2SO_4 and after various periods of time 10 ml. of 0.1 M. $\text{Pb}(\text{NO}_3)_2$. Then shaken. Ordinate of 16.2 indicates homogeneous distribution of lead through solid phase.

Fig. 2.

24 hours of aging in 0.005 M. barium nitrate than when fresh. After shaking of the fresh suspension with the lead nitrate for 6 to 7 days homogeneous mixed crystals (Ba-Pb-SO_4) were obtained, whereas this state of equilibrium was not yet reached after a month of shaking when the 24 hours old suspension was used.

Fig. 3 shows the speed of "penetration" of chromate into barium sulfate after various periods of aging. Apparently a very drastic aging has occurred after 24 hours in an excess of sulfate. Curves *D* and *B* in Fig. 3 indicate that the perfection has proceeded much further after 1 hours of aging in 0.005 M. sodium sulfate than after 24 hours in 0.005 M. barium nitrate. When the barium sulfate is aged in its saturated solution in water (equivalent body) its perfection occurs faster than in 0.005 M. sodium sulfate. (Fig. 4).

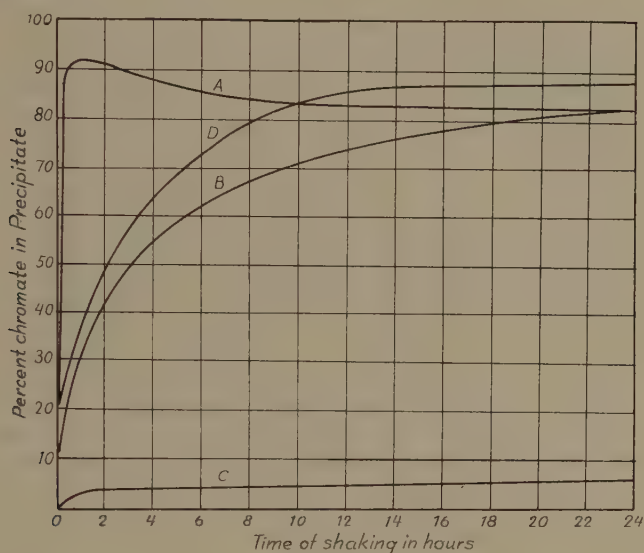


Fig. 3. Speed of Penetration of Chromate into Barium Sulfate: *A*. Fresh precipitate; *B*. 1 hour old precipitate aged in 0.005 M. sulfate; *C*. 24 hour old precipitate aged in 0.005 M. sulfate; *D*. 24 hour old precipitate aged in 0.005 M. barium.

In the studies of NOPONEN it was found again that all factors which decrease the solubility decrease the speed of perfection, and the reverse. From the facts that the specific surface did not change after 24 hours of aging in dilute barium solution whereas a distinct perfection occurred it is concluded that the recrystallization takes place in a liquid film around the primary particles. The surface of the latter is highly irregular and contains spots of varying activity. At these spots ions enter quickly into the liquid film, the solution being supersaturated with regard to more normal surface, where the lattice ions deposit again. The recrystallization, therefore, results in a kind of auto-digestion and auto-perfection of the primary particles (Fig. 1, I). The speed of recrystallization, especially during the early stages of the aging, is so great that the process is mainly confined to the liquid film around the particles, the ions in the supersaturated film having hardly an opportunity to enter into the bulk of the solution (which would cause Ostwald ripening) as they are deposited so quickly again. WM. VON FISCHER in this laboratory has shown that there is a tremendous difference

in the speed of solution of fresh lead sulfate and of a product aged for one day in the mother liquor. Upon shaking of 100 mg. of the fresh air-dried

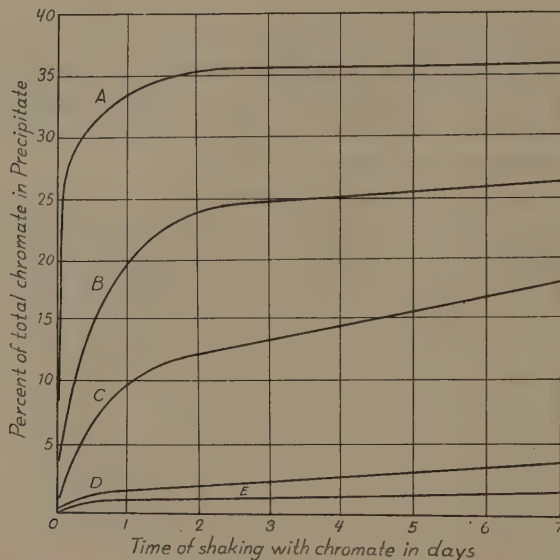


Fig. 4. A. Fresh precipitate; B. 1 hour old precipitate aged in 0.033 M. sulfate; C. 1 hour old precipitate aged as equivalent body; D. 24 hour old precipitate aged in 0.033 M. sulfate; E. 24 hour old precipitate aged as equivalent body.

lead sulfate in a glass stoppered bottle with 250 ml. of water at 25°C, the solution was slightly supersaturated with regard to lead sulfate after half a minute of shaking, upon longer periods of shaking the solubility decreased gradually until after several hours the normal solubility was found. On the other hand, upon shaking of 100 mg. of the one day old product with 250 ml. of water the solution was not yet saturated with regard to lead sulfate after one day.

From the work of G. E. NOPONEN ⁴⁾ and H. YUTZY ⁵⁾ to be published in the near future we arrive at the conclusion that *the speed of perfection is not determined by the solubility of the precipitate in the bulk of the solution, but by the solubility in the liquid film around the particle*. From Fig. 3 it is evident that barium sulfate ages much faster in 0.005 M. sodium sulfate than in 0.005 M. barium nitrate, whereas the fastest aging occurs in a medium containing neither an excess of barium nor of sulfate. (Fig. 4). The latter result was to be expected, since the solubility of barium sulfate under this condition is greater than in the presence of either of its ions. On the other hand, the solubility in 0.005 M. sulfate and 0.005 M. barium is of the same order, still the aging in the former case is much faster. This difference is attributed by us to the fact that barium ions are much stronger adsorbed than sulfate on barium sulfate. Consequently, the

⁵⁾ H. YUTZY Doctor's thesis, University of Minnesota, June, 1936.

solubility of barium sulfate in the liquid film around the particles is much smaller in a medium of 0.005 M. barium nitrate than of 0.005 M. sulfate.

Although the average particle size did not change after 24 hours of aging in 0.005 M. barium nitrate it was found that it decreased materially after aging for this period of time in 0.005 M. sulfate (for some figures, see table 1). Thus, not only drastic perfection occurs in the sulfate medium, but also a marked cementing of the particles (type 3 of aging). It is clear now that there is a relatively close relation between these two types of aging, as both of them are a result of the recrystallization (= perfection) process. Apparently the perfection is not always accompanied by a cementing process, as in the case of the aging of barium sulfate in 0.005 M. barium nitrate. Whether this is to be attributed to a repulsion of the particles by the presence of the adsorbed barium ions has not been investigated yet.

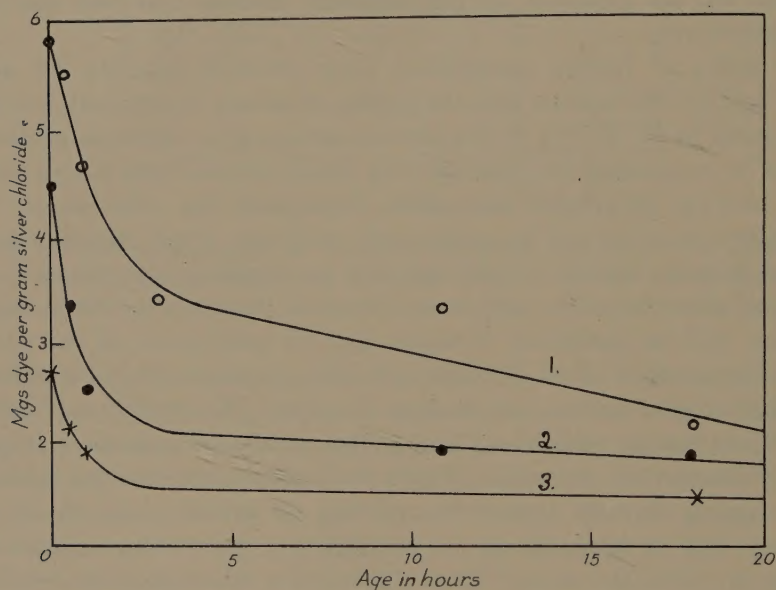
The aging of freshly precipitated silver chloride from 0.1 M. silver nitrate and 0.1 M. sodium chloride (order of mixing immaterial) has been investigated by H. YUTZY⁵⁾. An attempt was made to follow the perfection process by measuring the velocity with which bromide ions added to the liquid medium distributed themselves throughout the solid phase. The experiments were carried out under such conditions (high chloride content and low bromide content in solution) that no chemical precipitation (mass action) of silver bromide could occur. However, an extensive study, details of which will be published, revealed that the mechanism of the mixed-crystal formation of silver chloride and silver bromide was quite different from that of lead sulfate and thorium *B* sulfate (KOLTHOFF and ROSENBLUM³⁾) or barium sulfate and lead sulfate and barium chromate respectively (NOPONEN⁴⁾). It appeared that the bromide attacked the lattice of silver chloride directly (either by splitting off layers of mixed crystals relatively rich in bromide, or by developing a great many cracks and crevices to relieve the strain). Even a precipitate which had been aged for a year in the mother liquor was readily attacked by bromide in solution. Only when the initial bromide concentration in the solution was extremely small the mixed-crystals were formed in the normal way; i.e. the bromide was incorporated into the recrystallizing silver chloride by way of the liquid phase, a mechanism comparable to that of the cases discussed above. Unfortunately, this type of incorporation of bromide into the recrystallizing silver chloride occurs at such small bromide concentrations in the solution that the decrease of its concentration cannot be determined with sufficient accuracy. Still, it was possible to obtain conclusive evidence of the fact, that the speed of perfection of the silver chloride increased again with increasing solubility in the medium in which it was aged.

Preliminary experiments with the aid of Dr. D. H. HULL were carried out with artificial radioactive chlorine. The speed of distribution of the latter through silver chloride was investigated in a manner comparable to that of the thorium *B* through lead sulfate. Owing to great experimental

difficulties the results are of a preliminary character only, but showed definitely that the speed of distribution decreased fairly rapidly with increasing age of the silver chloride. Qualitatively, therefore, the aging of silver chloride seems comparable to that of barium and of lead sulfate in this respect.

The total surface of the aging silver chloride was measured with the aid of wool violet under such conditions that the surface was saturated with the dye. For the sake of brevity only a few of the results are plotted in Fig. 5.

The least aging as measured with the dye was found in 0.001 M. silver nitrate, more aging as an "equivalent body" (no excess of lattice ions in the solution) and the most pronounced aging in 0.001 M. sodium chloride.



Aging measured by Dye adsorption.

1. Aged in 0.001 M. Silver.
2. Aged as an equivalent body.
4. Aged in 0.001 M. chloride.

Fig. 5.

The latter result was unexpected, as the solubility of silver chloride in 0.001 M. chloride is less than in pure water: it is interpreted by us in the following way. In the first place it is well known that silver halides have a pronounced tendency to adsorb their own ions, the halide being more strongly adsorbed than the silver ions⁶). Thus the concentration of the (adsorbed) chloride in the solvated jacket around the particle may be much greater than in the bulk of the solution and may give rise to formation

⁶) Cf. E. J. W. VERWEY, Chem. Rev. 16, 363 (1935); I. M. KOLTHOFF and J. J. LINGANE, J. Am. Chem. Soc. 58, 1528 (1936).

of complex AgCl_2 ions. It is known ⁷⁾ that the solubility of silver chloride in stronger chloride solutions is greater than in water due to formation of complex argento-chloride ions. If the concentration of the adsorbed chloride ions in the liquid film is great enough, the solubility of the silver chloride in the liquid jacket around the particle may be much greater than in the bulk of the solution, and also greater than the solubility in pure water; thus accounting for the much more rapid aging in 0.001 M. sodium chloride than in water. It was shown that the aging is promoted by factors which increase the solubility (various concentrations of ammonia and of sodium chloride). Although the solubility of silver chloride in absolute ethanol is about 100 times smaller than in water, a rapid aging occurred when the fresh precipitate was kept in 0.001 M. lithium chloride in ethanol. Again, the complex formation may account for this result. When kept in 0.001 M. silver nitrate in absolute ethanol, the aging was found to be very slow.

This aging, as measured by the dye adsorption, is attributed to a cementing together of the particles (type 3), the latter in the case of silver chloride, having a great tendency to form agglomerates. This cementing together occurs simultaneously with the perfection process (type 1). If these types of aging occur rapidly in a flocculated sol, the flocculation process will be more or less irreversible, i.e. upon peptization after aging it will not be possible to obtain a sol with the same number of particles as the original one, even if complete peptization of a fresh flocculate occurred. With increasing age of the flocculate the process becomes less and less reversible, as the cemented agglomerates grow in size and the number of active spots, where the peptizing ions are adsorbed, decreases rapidly with increasing perfection. Precipitated silver chloride ages so rapidly that it can hardly be peptized again. With decreasing solubility of the colloidal particles the two types of aging become less rapid and peptization, as a rule, can be readily accomplished after short periods of time after the flocculation (silver iodide). Precipitates extremely slightly soluble in the liquid medium (hydrous ferric and other oxides) can be peptized after longer periods of aging.

The studies referred to above do not give a complete insight into the complex mechanism of the aging and more work is being done to investigate various phenomena. The results obtained so far permit the formulation of some of the above mentioned working hypotheses which are open to experimental tests.

Summary.

1. A distinction has been made between various types of aging.
2. The most important type of aging is a perfection process as a result of recrystallization in a liquid film around the crystalline particles. All

⁷⁾ G. S. FORBES and H. I. COLE, J. Am. Chem. Soc. **43**, 2492 (1921); J. KENDALL and C. H. SLOAN, J. Am. Chem. Soc. **47**, 2306 (1925).

factors increasing the solubility of the solid in the liquid film promote this type of aging, substances inhibiting the recrystallization inhibit the aging (adsorbed dyes).

3. When the primary particles of the precipitate form loose agglomerates the perfection may be accompanied by a cementing together of the particles to solid conglomerates (Fig. 1, III). The significance of this type of aging is discussed in connection with the peptization of flocculated colloids as a function of age.

4. The classical type of "Ostwald ripening" is of subordinate significance in the aging of slightly soluble precipitates at room temperature.

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